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“Oxidative Addition” of Halogens to Uranium(IV) Bis(amidophenolate) Complexes

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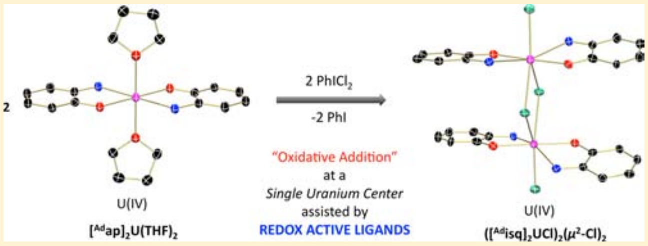
Supporting Information

ABSTRACT: A series of U(IV) complexes, $(^{R}ap)_2U(THF)_2$ [R = *tert*-butyl (*t*-Bu) (**1**), adamantyl (Ad) (**2**), diisopropylphenyl (dipp) (**3**)], supported by the redox-active 4,6-di-*tert*-butyl-2-(R)amidophenolate ligand, have been synthesized by salt metathesis of 2 equiv of the alkali metal salt of the ligand, $M_2[^{R}ap]$ [M = K (**1** and **2**), Na (**3**)], with UCl_4. Exposure of these uranium complexes to 1 equiv of $PhICl_2$ results in oxidative addition to uranium, forming the bis-(4,6-di-*tert*-butyl-2-(R)iminosemiquinone) $([^{R}isq]^{1-})$ uranium(IV) dichloride dimer, $[(^{R}isq)_2UCl]_2(\mu^2\text{-}Cl)_2$ [R = *t*-Bu (**4**), Ad (**5**), dipp (**6**)]. The addition of iodine to **1** forms $(^{tBu}isq)_2UI_2(THF)$ (**7**), while the reactivity of I_2 with **2** and **3** results in decomposition. Complexes **1**–**7** have been characterized by ^1H NMR and electronic absorption spectroscopies. X-ray crystallography was employed to elucidate structural parameters of **2**, **3**, **5**, and **7**.



■ INTRODUCTION

Oxidative addition is a ubiquitous organometallic transformation but is typically relegated to d-block transition metals that readily access two electron redox couples.[1,2] In contrast, uranium is known to primarily undergo single electron processes, and thus multiple metal centers are required to perform the analogous chemistry. An early example of multi-electron chemistry with uranium by Finke and co-workers illustrates the oxidative addition of a series of alkyl halides (RX) (RX = $C_6H_5CH_2Cl$, $(CH_3)_3CCH_2Cl$, $CH_2{=}CHCH_2CH_2Cl$, CH_3I, CH_3Br, $C_6H_5CH_2I$, *c*-$(C_3H_5)CH_2Cl$) to two molecules of trivalent Cp^*_2UCl (Cp^* = η^5-1,2,3,4,5-pentamethylcyclopentadienide). This results in R–X bond cleavage and one-electron oxidation of each center to U(IV), forming 0.5 equiv of $Cp^*_2UCl(X)$ and 0.5 equiv of $Cp^*_2UCl(R)$.[3] This work was extended by Ephritikhine et al., who demonstrated formation of Cp_3UX and Cp_3UR by addition of RX [RX = CH_3I, *n*-C_4H_9X (X = Cl, Br, I), *i*-C_3H_7Cl, $C_6H_5CH_2Cl$, $CH_2{=}CHCH_2Cl$, CH_3CN, C_6H_5CN] to 2 equiv of Cp_3U (Cp = η^5-C_5H_5).[4,5] More recently, Boncella and co-workers have reported oxidative addition of PhEEPh (E = S, Se, Te) to the uranium(V) bis(imido) dimer, $[U(N^tBu)_2I(^tBu_2bpy)]_2$ ($^tBu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl), produces the uranium(VI) derivatives, $[U(N^tBu)_2I(^tBu_2bpy)(EPh)]$, as well as $[U(N^tBu)_2I_2(^tBu_2bpy)]_2$ and $[U(N^tBu)_2(EPh)_2(^tBu_2bpy)]$.[6] Evans and co-workers have illustrated the activation of PhSSPh by the trivalent, dimeric hydride complex, $(Cp^*_2U)_2(\mu^2\text{-}H)_2$, resulting in the formation of the oxidized, tetravalent $Cp^*_2U(SPh)_2$ monomer.[7] These examples show that multi-electron chemistry can be achieved by one-electron oxidation of two uranium centers in concert.

The synthesis of f-block complexes capable of performing multi-electron reactions at a single metal center is important in establishing the utility of these elements for organometallic transformations. Such chemistry has been effectively demonstrated for first-row transition metals through the use of redox-active ligands (RAL),[8−15] which impart reactivity unto these elements similar to that of their precious metal counterparts. Likewise, redox-active ligands have been shown to facilitate multi-electron chemistry with lanthanides and actinides.[16] Fedushkin and co-workers have reported lanthanides (Ln = Sm, Yb, La) supported by α-diimine ligands are capable of performing one- and two-electron chemistry, including the reduction of halogens.[17] Low-valent uranium centers supported by RAL's, such as bridging η^6-aromatic rings,[18] bipyridine,[19−21] and pyridine(diimines),[22] have been shown to facilitate multi-electron processes by storing electrons for later use. Kiplinger and co-workers have reported and fully characterized the uranium acenaphthylene compounds, $(dpp\text{-}BIAN)_2U$ and $(dpp\text{-}BIAN)_2U(THF)$ (dpp-BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthylene), establishing these species as tetravalent uranium centers chelated by dianionic ligands.[23] Despite the reduced nature of these ligands, reactivity studies with these compounds were not possible due to decomposition.

Our laboratory has recently shown this chemistry can be extended to α-diimines with the synthesis of $(^{Mes}DAB^{Me})_2U(THF)$ [$^{Mes}DAB^{Me}$ = $ArN{=}C(Me)C(Me){=}NAr$; Ar = 2,4,6-trimethylphenyl (Mes)]. Upon metalation with uranium, the neutral α-diimine is reduced to the dianionic ene-diamide resonance form, generating the uranium(IV) product. This species can perform multi-electron reduction of the C–I bond bond in iodomethane (CH_3I), forming a new uranium-iodide

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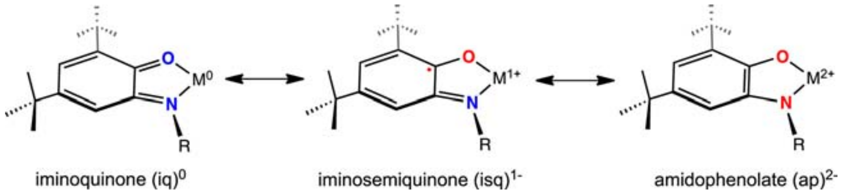
Chart 1. Resonance Structures of Amidophenolate Ligand Bound to a Metal in Various Oxidation States[a]



[a]Neutral heteroatoms are depicted in blue, and anionic heteroatoms are depicted in red.

bond and transferring the methyl group to the ene-diamide ligand to generate $(^{Mes}DAB^{Me})(^{Mes}DAB^{Me2})UI$.[24] The inability to transfer the methyl group to the uranium center prompted the investigation of *ortho*-aminophenol ligands, as these have been utilized by Heyduk and co-workers to facilitate oxidative addition of halogens (X_2; X = Cl, Br, I) to d^0, Group(IV) complexes, $(^{tBu}ap)_2M(THF)_2$ (M = Ti, Zr, Hf). One reducing equivalent from each ligand is transferred to the metal center, resulting in the formation of the bis(iminosemiquinone) species $(^{tBu}isq)_2MX_2$ (^{tBu}isq = 4,6-di-*tert*-butyl-2-(*tert*-butylimino)semiquinone), where both halides have been added to the central metal ion (Chart 1).[25,26] This seminal work illustrates the ability of amidophenolates to act as electron sources from which electron poor metals can draw, facilitating multi-electron reactivity at d^0 metals. We postulated that these ligands could support analogous processes for uranium centers by serving as electron sources, circumventing the otherwise necessary oxidation to 6+. Herein we present the synthesis and characterization of a family of uranium(IV) bis(amidophenolate) complexes and their reactivity toward oxidative addition of halogens.

■ EXPERIMENTAL SECTION

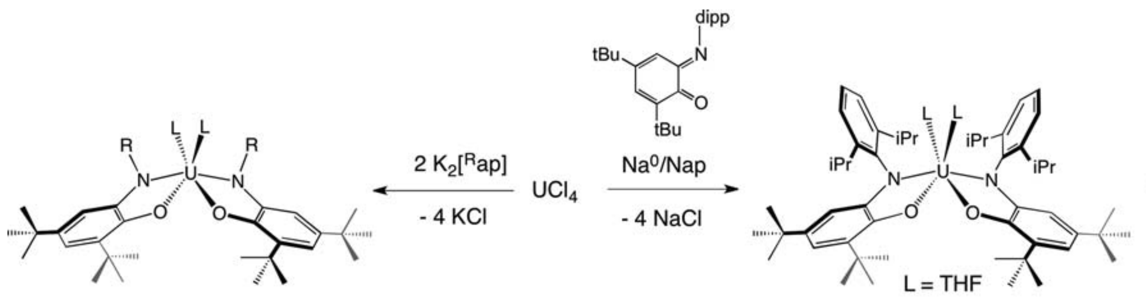
General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.[27] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze−pump−thaw cycles. Iodine was purchased from Sigma Aldrich and sublimed prior to use. 3,5-Di(*tert*-butyl)catechol and 1-aminoadamantane were purchased from Sigma Aldrich and used as received. Sodium metal in mineral oil was purchased from Sigma Aldrich and washed with dry pentane prior to use. Naphthalene was purchased from Fisher Scientific and dried on a Schlenk line overnight prior to use. Elemental analyses were performed by Midwest Microlab, LLC, in Indianapolis, IN (**1**, **3**, and **7**) and Complete Analysis Laboratories, Inc., in Parsippany, NJ (**2**, **4**−**6**). UCl_4,[28] KCH_2Ph,[29] 4,6-di-*tert*-butyl-2-(*tert*-butylamino)phenol ($H_2{}^{tBu}ap$),[30] 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]quinone (^{dipp}iq)[31] and $PhICl_2$[32] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 299.992 MHz. All chemical shifts were reported relative to the peak for $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained using an acquisition time of 0.5 s; thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half height in hertz, the integration value, and where possible, the peak assignment. Solid state infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrum RX I spectrometer. Samples were made by crushing the solids, mixing with dry KBr, and pressing into a pellet. Electronic absorption measurements were recorded at 294 K in THF in sealed 1 cm quartz cuvettes with a Jasco V-670 spectrophotometer. Single crystals of $(^{Ad}ap)_2U(THF)_2$ (**2**), $(^{dipp}ap)_2U(THF)_2$ (**3**), and $(^{tBu}isq)_2UI_2(THF)$ (**7**) for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å). Single crystals of $[(^{Ad}isq)_2UCl]_2(\mu^2\text{-}Cl)_2$ (**5**) were coated with polybutenes oil in a glovebox and quickly transferred to the goniometer head of a Nonius KappaCCD image plate diffractometer equipped with a graphite crystal, incident beam monochromator. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.[33] The structures were solved using the structure solution program PATTY in DIRDIFF99.[34] Refinement was performed on a LINUX PC using SHELX-97.[33] The data were collected at a temperature of 150(1) K.

Preparation of $(^{tBu}ap)_2U(THF)_2$ (1). A 20 mL scintillation vial was charged with UCl_4 (0.050 g, 0.132 mmol) and approximately 3 mL of THF, and was cooled to −35 °C. In a separate vial 4,6-di-*tert*-butyl-2-(*tert*-butylamino)phenol, $H_2[^{tBu}ap]$ (0.073 g, 0.265 mmol), was dissolved in 5 mL of THF. A solution of benzyl potassium (0.069 g, 0.526 mmol) in THF was added to the aminophenol dropwise with vigorous stirring, resulting in a bright yellow solution of the deprotonated ligand $K_2[^{tBu}ap]$, which was also cooled to −35 °C. The solution of deprotonated ligand was added to the uranium solution with stirring, resulting in a color change from pale green to dark, yellow-brown. After 30 min of stirring, THF was removed under reduced pressure. The product was dissolved in pentane and filtered over Celite to remove KCl. Upon removing pentane *in vacuo*, the product was isolated as a yellow-brown powder (0.090 g, 0.0964 mmol, 73%). Analysis for $C_{44}H_{74}N_2O_4U$: Calcd. C, 56.63; H, 7.99; N, 3.00. Found C, 56.94; H, 8.09; N, 2.90. ^{1}H NMR (C_6D_6, 25 °C): δ = −55.92 (250, 18H, $-C(CH_3)_3$), −40.24 (920, 8H, THF-CH_2), −25.07 (846, 8H, THF-CH_2), 10.94, (41, 18H, $-C(CH_3)_3$), 19.05 (51, 2H, CH), 38.14 (57, 18H, $-C(CH_3)_3$), 43.99 (46, 2H, CH).

Preparation of $H_2(^{Ad}ap)$. Outside of a glovebox, a 100 mL round-bottom flask was charged with 3,5-di(*tert*-butyl)catechol (3.00 g, 0.0135 mol) and an equivalent of 1-aminoadamantane (2.50 g, 0.0155 mol). The solids were dissolved in approximately 50 mL of toluene. Anhydrous $MgSO_4$ was added as a drying agent. The mixture was refluxed for 18 h, after which time the product was filtered. In a 500 mL separatory funnel, a solution of saturated sodium dithionate was added to the dark blue filtrate until the solution was bright green. The aqueous and organic layers were separated. After the organic layer was dried on a Schlenk Line overnight, the remaining solid was washed with diethyl ether, resulting in the isolation of the product as a white powder (2.182 g, 0.058 mol, 44%). ^{1}H NMR (C_6D_6, 25 °C): 1.42 (s, 9H, ^{t}Bu), 1.56 (br, s, 6H, Ad-CH_2), 1.59 (br, s, 6H, Ad-CH_2), 1.71 (s, 9H, ^{t}Bu), 1.88 (br, s, 6H, Ad-CH_2), 6.94 (d, J = 2 Hz, 1H, Ph−CH), 7.45 (d, J = 3 Hz, 1H, Ph−CH). IR = 3200 cm^{-1} (O−H), 3308 cm^{-1} (N−H).

Preparation of $(^{Ad}ap)_2U(THF)_2$ (2). A 20 mL scintillation vial was charged with $(^{Ad}ap)H_2$ (0.080 g, 0.219 mmol) and approximately 5 mL



R = tBu (1), Ad (2)

3

(1)

of THF. In a separate vial, 2 equiv of benzyl potassium (0.057 g, 0.435 mmol) was dissolved in 6 mL of THF. The orange solution of KCH_2Ph was added to the clear slurry of (^{Ad}ap)H_2 with vigorous stirring, resulting in a bright yellow solution. After 30 min of stirring, the ligand salt was cooled to −35 °C. In a separate vial, half an equivalent of UCl_4 (0.041 g, 0.109 mmol) was dissolved in THF and cooled to −35 °C. With vigorous stirring, K_2[^{Ad}ap] was added to the uranium solution resulting in immediate darkening of the solution to orange-brown. The solution was brought to room temperature and stirred for an additional 10 h. Solvents were removed under reduced pressure. The brown orange residue was dissolved in diethyl ether and filtered over Celite to remove KCl. Solvents were removed under reduced pressure. The product was recrystallized from a concentrated solution of pentane and THF (3:1 ratio) at −35 °C, resulting in the isolation of an orange powder (0.086 g, 0.080 mmol, 73%). Orange, plate-shaped crystals suitable for X-ray analysis were grown from a solution of pentane and THF (2:1 ratio) overnight at −35 °C. Analysis for $C_{60}H_{90}N_2O_4U$: Calcd. C, 68.37; H, 6.58; N, 2.13. Found C, 68.19; H, 6.65; N, 2.14. ^{1}H NMR (C_6D_6, 25 °C): δ = −70.59 (340, 6H, Ad-C*H*), −63.21 (260, 6H, Ad-C*H*), −25.58 (1650, 8H, THF-CH_2), −18.93 (71, 6H, Ad-C*H*), −12.68 (140, 6H, Ad-C*H*), −12.47 (130, 6H, Ad-C*H*), 0.02 (2180, 8H, THF-CH_2), 10.71 (60, 18H, −C(C*H*)$_3$), 18.55 (59, 2H, −C*H*), 37.94 (69, 18H, −C(C*H*)$_3$), 43.56 (55, 2H, −C*H*).

Preparation of (^{dipp}ap)$_2$U(THF)$_2$ (3). A 20 mL scintillation vial was charged with 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]-quinone, ^{dipp}iq (0.100 g, 0.262 mmol), sodium metal (0.020 g, 0.870 mmol), and a catalytic amount of naphthalene. After stirring for 24 h, the color of the solution had progressed from the red-brown of the oxidized ligand, through the bright-blue monoreduced ligand to pale yellow-green for the sodium salt of the amidophenolate ligand, Na_2(^{dipp}ap). A separate vial was charged with UCl_4 (0.050 g, 0.132 mmol) and approximately 3 mL of THF and cooled to −35 °C. The solution of reduced ligand was added dropwise to the pale green UCl_4 solution with vigorous stirring. A color change to orange-brown was observed immediately; however, to ensure complete conversion, the reaction mixture was stirred for 10 h. After removing THF under reduced pressure, the product was extracted with pentane and filtered over Celite to remove the byproduct, NaCl. Complex **3** was recrystallized from a concentrated pentane solution and was isolated as a red-orange solid (0.118 g, 0.092 mmol, 71%). Crystals suitable for X-ray analysis were grown from a concentrated pentane solution. Analysis for $C_{56}H_{82}N_2O_3U$: Calcd. C, 62.90; H, 7.73; N, 2.62. Found C, 62.86; H, 7.55; N, 2.55. ^{1}H NMR (C_6D_6, 25 °C): δ = −24 (800), −14 (600), −11 (950), 2 (900), 6 (540), 15 (1100), 19 (1100). Because of the broadness of the ^{1}H NMR spectrum at 25 °C, chemical shifts are reported without decimal places, and peak widths at half height are reported to two significant figures.

Preparation of (^{tBu}isq)$_2$UCl$_2$ (4) and (^{Ad}isq)$_2$UCl$_2$ (5). A 20 mL scintillation vial was charged with (^{R}ap)$_2$U(THF) (R = *t*-Bu, 0.050 g, 0.058 mmol; Ad, 0.050 g, 0.045 mmol) and approximately 3 mL of THF. In a separate vial, an equivalent of $PhICl_2$ (R = *t*-Bu, 0.016 g, 0.058 mmol; Ad, 0.013 g, 0.047 mmol) was dissolved in THF. The resulting pale yellow solution was added dropwise to the uranium solution, resulting in an instantaneous color change to dark green. After 5 min of stirring, solvents were removed under reduced pressure. The product was washed with pentane leaving a green solid.

Characterization of [(^{tBu}isq)$_2$UCl]$_2$(μ^2-Cl)$_2$ (4). Yield = 0.041 g, 0.024 mmol, 83%. Analysis for $C_{29}H_{58}N_2O_2UCl_2$: Calcd. C, 50.29; H, 6.80; N, 3.26. Found C, 50.16; H, 6.80; N, 3.26. ^{1}H NMR (C_6D_6, 25 °C): δ = 11.45 (104, 2H, Ar−C*H*), 20.69 (7, 18H, −C(CH_3)$_3$), 30.93 (46, 2H, Ar−C*H*), 56.54 (50, 18H, −C(CH_3)$_3$). UV−vis = 711 nm (635 M^{-1} cm^{-1}).

Characterization of [(^{Ad}isq)$_2$UCl]$_2$(μ^2-Cl)$_2$ (5). Yield = 0.056 g, 0.025 mmol, 86%. Crystals suitable for X-ray analysis were grown from a dilute pentane solution. Analysis for $C_{60}H_{90}N_2O_2UCl_2$: Calcd. C, 64.78; H, 5.67; N, 2.25. Found C, 64.59; H, 5.72; N, 2.14. ^{1}H NMR (C_6D_6, 25 °C): δ = 21.72 (6, 18H, −C(CH_3)$_3$), 56.74 (59, 18H, −C(CH_3)$_3$). UV−vis = 708 nm (613 M^{-1} cm^{-1}).

Preparation of [(^{dipp}isq)$_2$UCl]$_2$(μ^2-Cl)$_2$ (6). A 20 mL scintillation vial was charged with **3** (0.100 g, 0.094 mmol) and approximately 2 mL of diethyl ether. In a separate vial, an equivalent of $PhICl_2$ (0.026 g, 0.095 mmol) was dissolved in approximately 5 mL of THF. The pale yellow solution was added to the uranium compound, resulting in a darkening of the solution. After 5 min of stirring at room temperature, solvents were removed under reduced pressure. The resulting dark brown oil was dissolved in diethyl ether. The product, (^{dipp}isq)$_2$UCl$_2$, was isolated as a brown powder by recrystallization from a concentrated solution of diethyl ether layered with pentane (0.038 g, 0.018 mmol, 38%). Because of the instability of complex **6**, elemental analysis could not be obtained. ^{1}H NMR (C_6D_6, 25 °C): δ = −101.70 (54, 2H), −22.41 (57, 4H), −2.68 (34, 12H, −CH(CH_3)$_2$), 2.74 (33, 18H, −C(CH_3)$_3$), 7.47 (54, 2H), 20.06 (45, 18H, −C(CH_3)$_3$), 35.43 (43, 4H), 43.42 (73, 2H) . UV−vis = 742 nm (449 $M^{-1}cm^{-1}$).

Preparation of (^{tBu}isq)$_2$UI$_2$(THF) (7). A 20 mL scintillation vial was charged with (^{tBu}ap)$_2$U(THF) (0.050 g, 0.058 mmol) and approximately 3 mL of THF. In a separate vial, I_2 (0.014 g, 0.055 mmol) was dissolved in 2 mL of THF, and subsequently added dropwise to the uranium solution. An immediate color change to dark brown was observed. After solvents were removed under reduced pressure, the product was washed with cold pentane, resulting in a dark brown powder (0.051 g, 0.046 mmol, 86%). Crystals suitable for X-ray analysis were grown from a concentrated THF solution layered with pentane (1:1). Analysis for $C_{40}H_{66}N_2O_3I_2U$: Calcd. C, 43.10; H, 5.97; N, 2.51. Found C, 42.70; H, 5.85; N, 2.20. ^{1}H NMR (C_6D_6, 25 °C): δ = 18.38 (9, 2H, Ar−C*H*), 19.52 (7, 18H, −C(CH_3)$_3$), 21.75 (9, 2H, C*H*), 60.92 (45, 18H, −C(CH_3)$_3$).

■ RESULTS AND DISCUSSION

Synthesis and Characterization (^{R}ap)$_2$U(THF)$_2$. Initial experiments were aimed toward the synthesis of a family of bis(amidophenolate) complexes. Metalation of the *tert*-butylamidophenolate ligand, H_2[^{tBu}ap], was accomplished by first deprotonating the ligand with 2 equiv of benzyl potassium. Addition of this yellow-orange solution to one-half equivalent of a green THF solution of UCl_4 at −35 °C caused an immediate color change to yellow brown (eq 1). After workup, the product, (^{tBu}ap)$_2$U(THF)$_2$ (**1**), was isolated by recrystallization from pentane. Analysis of the product by ^{1}H NMR

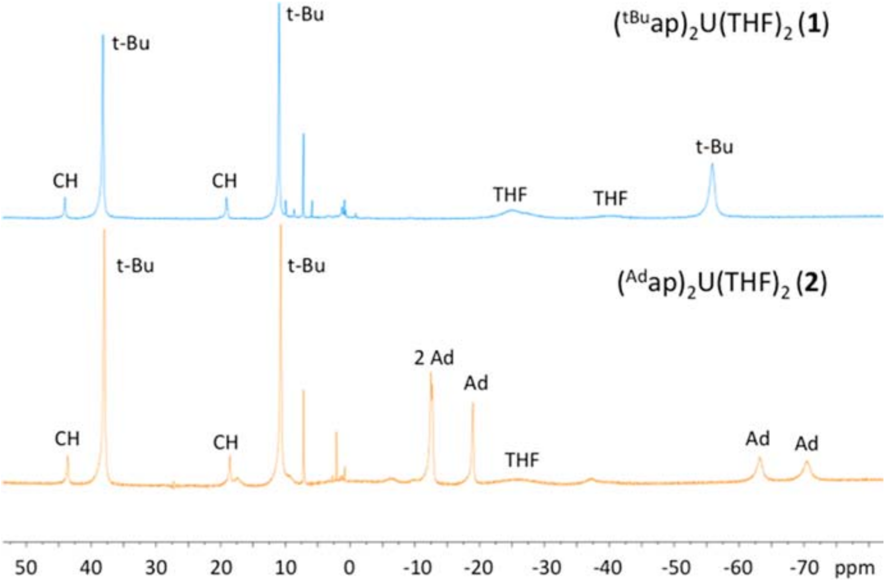


Figure 1. ^{1}H NMR spectra (C_6D_6, 25 °C) of **1** (top) and **2** (bottom).

spectroscopy revealed seven paramagnetically shifted and broadened resonances, ranging from −55.92 to 43.99 ppm (Figure 1, top). Three diagnostic signals integrating to 18H each were located at −55.92, 10.94, and 38.14, corresponding to the three sets of two chemically equivalent *t*-Bu groups of the amidophenolate ligand. Two resonances are visible for the aryl protons of the amidophenolate ligand, as well as two signals (8H each) for the protons of the two coordinated THF ligands. Compound **1** is analogous to the Group(IV) derivatives, $(^{tBu}ap)_2M(THF)_2$, synthesized by Heyduk et al.[25,26]

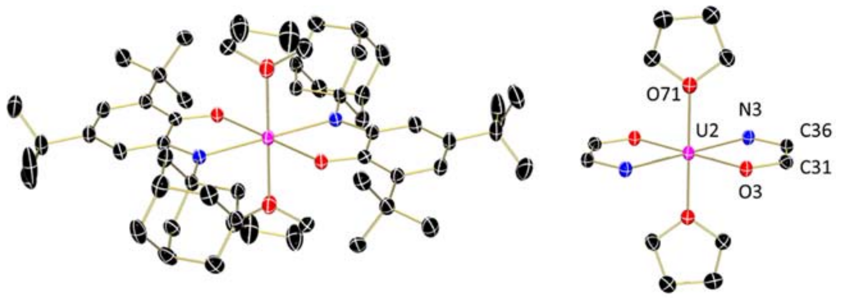
The sterically hindered aminophenol with an adamantyl amino substituent was also synthesized. Generation of this ligand was accomplished by refluxing 1 equiv of 1-adamantylamine with 3,5-di(*tert*-butyl)catechol in toluene over magnesium sulfate. After workup, the product, $H_2[^{Ad}ap]$, was isolated in moderate yields and characterized by ^{1}H NMR and IR spectroscopies, confirming the formation of the desired aminophenol. Metalation of this ligand was performed in analogy to the *tert*-butyl derivative, eventually forming an orange solution when 2 equiv of $K_2[^{Ad}ap]$ was added to UCl_4 in THF (eq 1). After workup, the product, $(^{Ad}ap)_2U(THF)_2$ (**2**), was characterized by ^{1}H NMR spectroscopy. The spectrum revealed 11 paramagnetic signals located between −70.59 and 43.56 ppm, consistent with the formation of **2** (Figure 1, bottom). Two resonances integrating to 18H each at 10.71 and 37.94 were assigned as the *t*-Bu groups, while two signals at 18.55 and 43.56 ppm match the aryl-C*H* protons of the aminophenol ligand framework. The aryl resonances have chemical shifts similar to those in the *tert*-butyl uranium complex, indicating similarities in the chemical environment. Five additional resonances were located upfield for the adamantyl protons, whereas two extremely broad signals were assigned to the THF ligands in **2**.

To confirm the formation of **2**, orange plate crystals suitable for X-ray analysis were grown from a concentrated solution of pentane and THF (3:1) at −35 °C overnight. Refinement of the data revealed co-crystallization of two independent, six coordinate isomers of the product, $(^{Ad}ap)_2U(THF)_2$, in both the *cis*-THF (**2-*cis***) ($O_{THF}UO_{THF}$ = 82.08(14)°) and *trans*-THF (**2-*trans***) ($O_{THF}UO_{THF}$ = 179.99(2)°) forms (Figure 2, Table 1). Compound **2-*cis*** has a pseudo-octahedral geometry around uranium. The oxygen atoms of each amidophenolate ligand are *trans* to each other (OUO = 164.70(12)°), while the nitrogen atoms of each ligand are *cis* to one another (NUN = 108.63(13)°) and *trans* to a THF molecule (NUO_{THF} = 149.36(12)°, 148.09(12)°). The structure of **2-*cis*** is analogous to that of the Group(IV) derivatives, $(^{tBu}ap)_2M(THF)_2$ (M = Ti, Zr, Hf).[25,26] Complex **2-*trans*** has an octahedral geometry, with uranium located on a center of inversion within the unit cell. This coordination geometry of the amidophenolate ligands is comparable to that of the square planar Co(III) species, $[Cp_2Co][Co(^{Ph}ap)_2]$, reported by Soper and co-workers.[35]

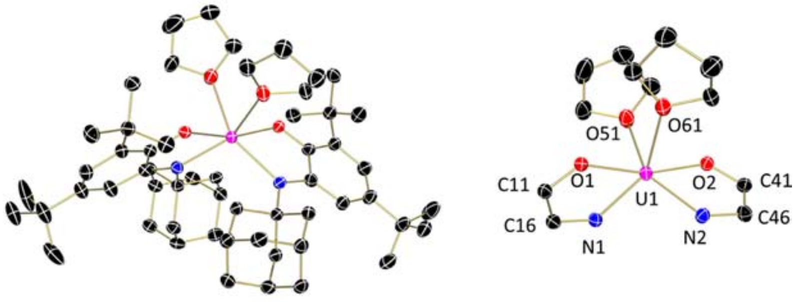
As X-ray crystallography is often employed to establish metrical parameters for ligand oxidation state assignment, analysis of the intraligand bond distances and lengths between uranium and heteroatom of complexes **2-*cis*** and **2-*trans*** were examined. The U−N (2.334(4)−2.381(3) Å) and U−O (2.163(3)−2.174(3) Å) bond distances compare favorably to tetravalent, anionic uranium amide[36] and alkoxide[37] distances. Furthermore, the O−C (1.360(5) and 1.365(6) Å) and N−C (1.394(6) and 1.412(6) Å) bond lengths compare favorably to those reported for $(^{tBu}ap)_2M(THF)_2$, supporting retention of the dianionic oxidation state of the amidophenolate ligand.[25,26]

Observation of the two geometric isomers of compound **2** indicated that the broadness noted in the ^{1}H NMR spectrum may be due in part to interconversion between *cis* and *trans* isomers on the NMR time scale. On the basis of the similar spectroscopic features of **1** and **2**, it was postulated that a similar process occurs for **1** as well. Acquisition of the ^{1}H NMR spectrum of both **1** and **2** at −35 °C confirmed THF exchange in solution, as the broad resonances assigned to THF protons resolve into distinct resonances for both compounds upon cooling.

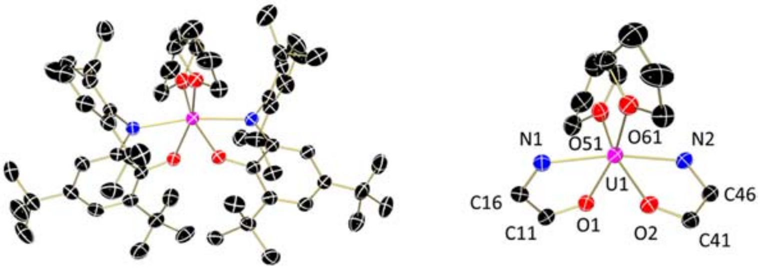
Following the successful formation and characterization of the aliphatic bis(amidophenolate) derivatives, we set out to synthesize the diisopropylphenyl analogue, $(^{dipp}ap)_2U(THF)_2$, to determine what effect, if any, an electron withdrawing amido substituent would have on subsequent reactivity. The analogous compound to **1** and **2** was formed by the reduction of 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]quinone (^{dipp}iq) *in*



$(^{Ad}ap)_2U(THF)_2$ (**2-*trans***)



$(^{Ad}ap)_2U(THF)_2$ (**2-*cis***)



$(^{dipp}ap)_2U(THF)_2$ (**3**)

Figure 2. Molecular structure of **2-*trans*** (top), **2-*cis*** (middle), and **3** (bottom) shown with 30% probability ellipsoids. Solvent molecules and hydrogen atoms have been removed for clarity. Right column shows the core of the molecules.

Table 1. Structural Parameters of 2-*trans*, 2-*cis*, and 3

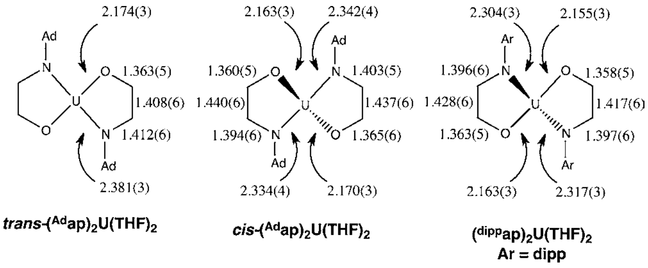
	2-*trans*		2-*cis*	3
		Bond Lengths (Å)		
U2−O3	2.174(3)	U1−O1	2.163(3)	2.163(3)
U2−N3	2.381(3)	U1−N1	2.334(4)	2.304(3)
		U1−O2	2.170(3)	2.155(3)
		U1−N2	2.342(4)	2.317(3)
U2−O71	2.412(3)	U1−O51	2.472(4)	2.482(3)
		U1−O61	2.475(3)	2.505(3)
O3−C31	1.363(5)	O1−C11	1.360(5)	1.363(5)
N3−C36	1.412(6)	N1−C16	1.394(6)	1.396(6)
		O2−C41	1.365(6)	1.358(5)
		N2−C46	1.403(5)	1.397(6)
		Bond Angles (deg)		
O3−U2−O3a	179.990(10)	O1−U1−O2	164.70(12)	90.31(11)°
N3−U2−N3a	179.998(2)	N1−U1−N2	108.63(13)	169.48(12)°
O71−U1−O71a	179.999(2)	O51−U1−O61	82.08(14)	109.25(11)°

situ using 2 equiv of Na^0 and a catalytic amount of naphthalene over 24 h. Upon addition of the solution of reduced ligand to one-half equivalent of UCl_4 at −35 °C, an orange solution resulted (eq 1). After workup and recrystallization from pentane, the product, $(^{dipp}ap)_2U(THF)_2$ (**3**), was isolated as a red-orange powder.

Analysis of **3** by ^{1}H NMR spectroscopy revealed seven extremely broad resonances ranging from −24.54 to 22.13 (Figure S1, Supporting Information). The signals corresponding to single aryl-protons of the ligand were not observed, perhaps due to the dynamic nature of **3** at 25 °C. Thus, complex **3** was analyzed by variable-temperature ^{1}H NMR spectroscopy. Cooling the sample to −35 °C resolved the broad resonances into distinct signals; however, the spectrum was not suitable for assignment of the product. Peak widths for the resonances of complex **3** at ambient temperature are consistent with that of the bis(ene-diamide) complex, $(^{Mes}DAB^{Me})_2U(THF)$, which also shows broad signals due to dynamic processes on the NMR time scale.[24]

To confirm the formation of the bis(amidophenolate) product, **3**, structural characterization was obtained via X-ray crystallography. Crystals suitable for analysis were grown from a concentrated pentane solution at −35 °C. Refinement of the data revealed a six-coordinate uranium center in a pseudo octahedral geometry (Figure 2, Table 1). The U−N distances of 2.305(3) and 2.317(3) Å and the U−O distances of 2.155(3) and 2.163(3) Å are indicative of monoanionic uranium-heteroatom linkages,[36,37] and compare favorably to the respective distances of **2**-***cis*** and **2**-***trans***, as summarized in Chart 2. Two dianionic ligands support the assignment of the oxidation state of uranium as tetravalent. Each ligand has been reduced by two electrons, as confirmed by the elongated C−N (1.396(6) and 1.397(6) Å) and C−O (1.363(5) and 1.358(5) Å) distances, from the values reported for the oxidized free ligand, ^{dipp}iq (C═N: 1.287(2), C═O: 1.221(6) Å).[31]

Chart 2. Comparison of Ligand Bond Distances (Å) between Complexes 2-*trans*, 2-*cis*, and 3



The structure of **3** also shows the THF in a *cis* configuration, with an $O_{THF}UO_{THF}$ angle of 109.25(11)°, similar to that of **2**-**cis** (82.08(14)°) and $(^{tBu}ap)_2M(THF)_2$ (M = Ti (83.23(8)°), Zr (84.14(12)°), Hf (83.72(8)°), synthesized by Heyduk and co-workers.[25,26] The coordination mode of the amidophenolates in **3** differs from **2**-***cis***, and the Group(IV) analogues as the nitrogen donors are *trans* to one another with an N−U−N angle of 169.48(12)°, while the oxygen atoms are *cis*, with an O−U−O angle of 90.31(11)°. In the case of **2**-**cis** and $(^{tBu}ap)_2M(THF)_2$, this trend is reversed [OUO = 164.70(12)°, NUN = 108.63(13)°; O−M(IV)−O ≅ 160°, N−M(IV)−N ≅104° (M = Ti, Zr, Hf)].

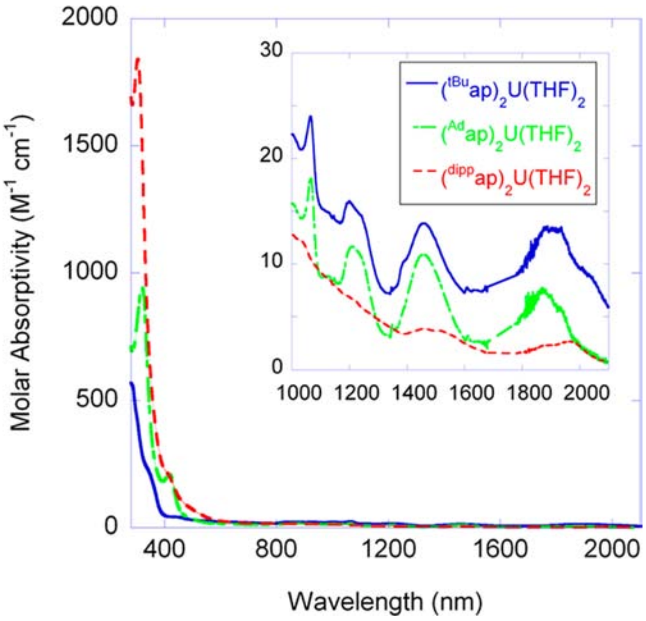
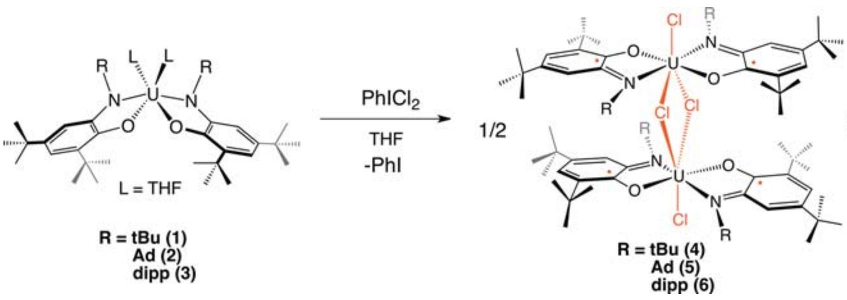


Figure 3. Electronic absorption spectra of **1** (red), **2** (blue), and **3** (green) in THF at ambient temperature. The inset shows the near-infrared region of the spectra. Solvent overtones have been removed between 1600 and 1800 nm.

The electronic absorption spectra of the bis(amidophenolate) complexes, **1**−**3**, were obtained in THF at ambient temperature, between 280 and 2100 nm (Figure 3). In the case of the aliphatic derivatives, $(^{R}ap)_2U(THF)_2$ (R = *t*-Bu, Ad), the near-infrared region of the spectra revealed a series of sharp but weak bands consistent with f−f transitions for a tetravalent uranium center.[23,24,38] For the aryl derivative **3**, these transitions are more broad and significantly weaker (4−20 M^{-1} cm^{-1}) than **1** and **2**. The spectrum is dominated by an intense charge transfer band at 280 nm (~580 M^{-1} cm^{-1}) with a shoulder located at 327 nm (~200 M^{-1} cm^{-1}) for complex **1**, consistent with the Group(IV) bis(amidophenolate) complexes, $(^{tBu}ap)_2M(THF)_2$ (M = Ti, Zr, Hf).[25,26] Similar spectroscopic features are also observed for **2**; however, these bands are red-shifted and more well-defined than that of complex **1**, highlighted in the transition at 418 nm (210 M^{-1} cm^{-1}) that no longer appears as a shoulder of the band at 320 nm (950 M^{-1} cm^{-1}) for the adamantyl species. In the case of complex **3**, the corresponding, intense feature at 312 nm (1800 M^{-1} cm^{-1}) dominates the high-energy region of the spectrum, but no shoulder is observed.



(2)

"Oxidative Addition" of Halogens. The reactivity of **1**−**3** toward halogens was evaluated to determine if amidophenolate ligands are capable of serving as electron sources to facilitate oxidative addition at a single uranium center, as has been shown by Heyduk and co-workers for Group(IV), d^0 metal centers.[25,26] Addition of 1 equiv of $PhICl_2$ to an aliphatic bis(amidophenolate) complex (**1** or **2**) results in an immediate color change to green (eq 2), analogous to those observed in the oxidation of $(^{tBu}ap)_2M$ to $(^{tBu}isq)_2MX_2$.[25,26] After solvents were removed under reduced pressure, the product was purified by washing with pentane. Analysis of these pentane washings by ^1H NMR spectroscopy showed signals for PhI, indicating successful chlorine atom transfer from the substrate. ^1H NMR spectroscopy showed a paramagnetic product, indicating the amidophenolate ligands were the source of the electrons used for oxidative addition to form the iminosemiquinone species, $[(^{R}isq)_2UCl]_2(\mu^2\text{-}Cl)_2$ [R = *t*-Bu (**4**), Ad (**5**)]. If the uranium served as the reductant, the resulting product would be hexavalent and thus diamagnetic.

To confirm the formation of the oxidative addition product, crystals of **5** were grown from dilute pentane at room temperature. X-ray diffraction showed a seven-coordinate uranium dimer, bridged by two chlorides, $[(^{Ad}isq)_2UCl]_2(\mu_2\text{-}Cl)_2$ (**5**) (Figure 4, Table 2), with a center of inversion located between the two Cl atoms in the plane bisecting the uranium centers. The terminal U−Cl distance of 2.636(2) Å compares favorably to tetravalent uranium chloride complexes, including $U[\eta^5\text{-}C_5H_4(CH_2Ph)]_3Cl$ (2.627(2) Å),[39] $(dmpe)_2UCl_4$ (dmpe = 1,2-bis(dimethylphosphino)ethane) (2.6480(13) Å),[40] $[UCl_2(acac)_2(THF)_2]$ (acac = $CH_3COCHCOCH_3$) (2.684(3) Å),[41] and $(Cp^*)_2U(\eta^2\text{-}(N_2)\text{−}CH_3\text{−}N\text{−}N{=}CPh_2)(Cl)$ (2.632(2) Å).[42] Comparatively, the U−Cl distances of the chlorines bridging the uranium centers have the expected elongated bond distances of 2.8037(16) and 2.8172(16) Å and resemble those for other tetravalent uranium dimers, including $[U(Me_3SiN\{CH_2CH_2NSiMe_3\}_2(\mu\text{-}Cl)_2]_2$ (2.811(1) Å),[43] $[UCl(\mu\text{-}L)U(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (L = $(CyN)_2C{=}N\text{−}N{=}C(NCy)_2$) (2.786(3) and 2.846(3) Å),[44] $[U(BIPM^{TMS}H)(Cl)_2(\mu\text{-}Cl)]_2$ ($BIPM^{TMS}$ = $C(PPh_2NSiMe_3)_2$) (2.8333(12) Å),[45] and $[U(\eta^6\text{-}C_6Me_6)Cl_2]_2(\mu\text{-}Cl)_3[AlCl_4]$ (2.75(5) Å).[46]

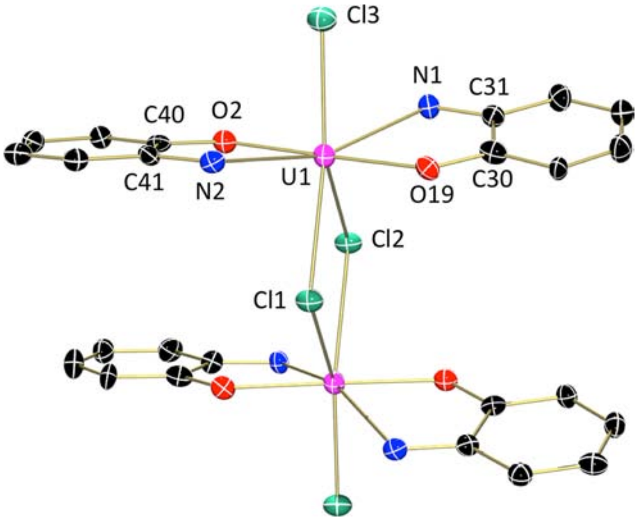


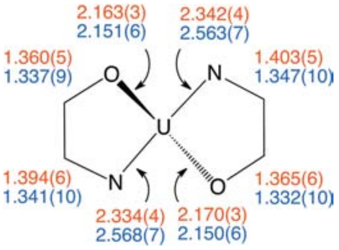
Figure 4. Molecular structure of **5** shown with 30% probability ellipsoids. Adamantyl and *tert*-butyl substituents have been removed to show the core of the molecule. Solvent molecules and hydrogen atoms have been removed for clarity.

Table 2. Molecular Structures of 5 and 7

	5 (X = Cl)	**7** (X = I)
	Bond Lengths (Å)	
U1−N1	2.568(7)	2.567(14)
N1−C31	1.341(10)	1.347(19)
U1−O19	2.151(6)	2.164(10)
O19−C30	1.337(9)	1.283(18)
U1−N2	2.563(7)	2.514(12)
N2−C41	1.347(10)	1.385(18)
U1−O2	2.150(6)	2.160(10)
O2−C40	1.332(10)	1.310(15)
U1−X1	2.8172(16)	3.1172(11)
U1−X2	2.8037(16)	3.1320(10)
U1−Cl3	2.636(2)	
	Bond Angles (deg)	
X1−U1−X2	69.84(6)	147.72(3)
Cl1−U1−Cl3	146.42(7)	
Cl2−U1−Cl3	143.70(7)	
N1−U1−N2	160.2(2)	153.7(4)
O1−U1−O2	179.0(2)	176.9(4)
U1−O31		2.486(10)

Oxidation of the amidophenolate ligand to the iminosemiquinone is evident in the lengthening of the U−N distances (2.563(7) and 2.568(7) Å) as compared to **2** (Chart 3), which are now consistent with a dative U−N interaction. The adjacent N−C bonds are contracted (1.341(10) and 1.347(10) Å), indicating an increase in π-bonding character of the C−N moiety as is expected for ligand oxidation to the iminosemiquinone species. The U−O distances (2.151(6) and 2.150(6) Å) and C−O distances (1.332(10) and 1.337(9) Å) are the same within error as the starting material, **2**, showing the anionic bond is maintained. These bond distortions within the product as compared to **2** are consistent with ligand oxidation to the monoanionic iminosemiquinone, $[isq]^{-1}$ and closely resemble the intraligand bond distances of $(^{tBu}isq)_2MX_2$.[25,26]

Chart 3. Comparison of Bond Distances (Å) for 2-*cis* (red) and 5 (blue)



Insight into the electronic structure and oxidation states of **4** and **5** was obtained by electronic absorption spectroscopy. Spectra were collected from 280 to 2100 nm in THF at ambient temperature (Figure 5). For both complexes, the near-infrared regions of the spectra contain a series of sharp bands with low intensity (50−175 M^{-1} cm^{-1}) consistent with uranium(IV) complexes.[38] In the visible region, broad, color-producing bands centered at 711 nm (**4**; 635 M^{-1} cm^{-1}) and 708 nm (**5**; 613 M^{-1} cm^{-1}) are noted. Similar absorptions have been observed in Heyduk's Group(IV) $[^{tBu}isq]_2MX_2$ complexes and are assigned as the π−π* transitions of the radical

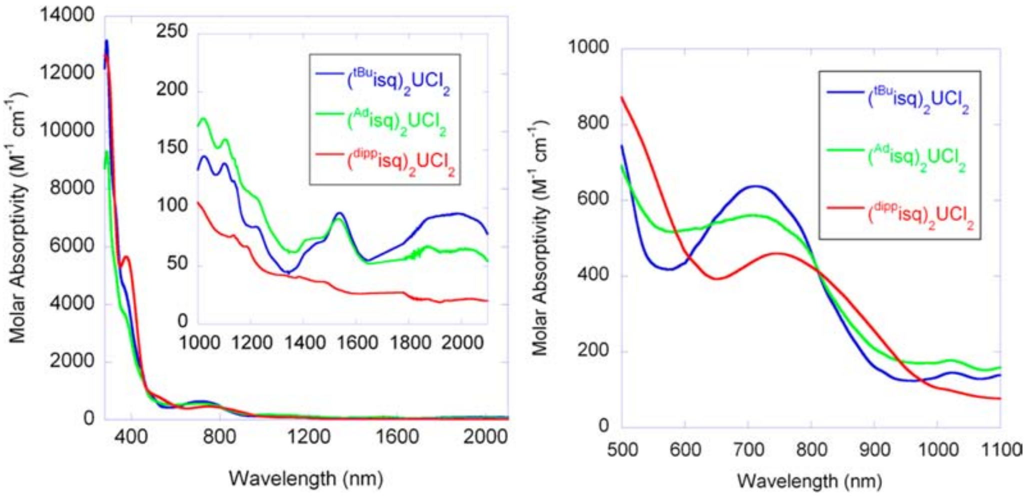
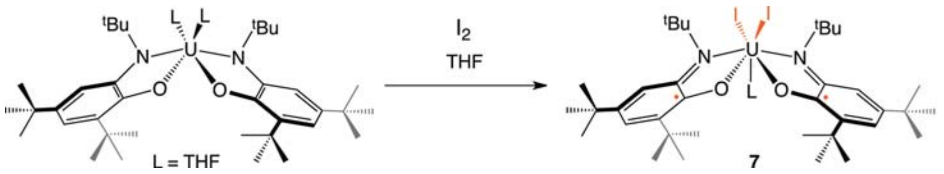


Figure 5. Electronic absorption spectra of **4** (blue), **5** (green), and **6** (red) in THF at ambient temperature. The inset shows the near-infrared region of the spectra. Solvent overtones are present between 1600 and 1800 nm.



(3)

iminosemiquinone ligands.[25,26] These bands for **4** and **5** are blue-shifted approximately 50 nm from the corresponding band of $(^{tBu}isq)_2HfCl_2$ (760 nm). Shifts of similar magnitude occur as Group(IV) is descended, as in the case of moving from Zr (789 nm) to Hf. Structural and spectroscopic data confirm the assignment of **4** and **5** as the products of oxidative addition of Cl_2, iminosemiquinone uranium(IV) dichloride species. It is evident that the electrons used for bond cleavage are derived from the amidophenolate ligands and not the uranium center, despite the fact that the 6+ oxidation state is accessible.

The oxidative addition chemistry of complex **3** was explored in analogy to that of **1** and **2** to compare the reactivity of a bis(amidophenolate) complex with an electron withdrawing, aryl-amido substituent. In the case of **3**, addition of an equivalent of $PhICl_2$ to the bis(amidophenolate) complex did not yield the aforementioned intense green color; instead a darkening of the solution was observed. After 5 min of stirring, solvents were removed under reduced pressure, and the product was isolated via recrystallization from a concentrated pentane and diethyl ether (1:1 ratio) solution. Analysis by ^1H NMR spectroscopy revealed a spectrum similar to that of **4** and **5**, with the expected eight paramagnetic resonances for the product of oxidative addition, "$[^{dipp}isq]_2UCl_2$" (**6**), ranging from −101.70 to 43.42 ppm. Complex **6** is fleeting, rapidly decomposing to multiple unidentified paramagnetic products in noncoordinating solvents.

To verify the presence of the iminosemiquinone radical in **6**, the electronic absorption spectrum was acquired and compared to that of complexes **4** and **5** (Figure 5). A band assigned as the open shell, $\pi-\pi^*$ transition is located at 742 nm (~500 M^{-1} cm^{-1}). This feature is significantly red-shifted from the aliphatic derivatives, **4** and **5**, due to the substitution of the diisopropylphenyl group, which extends the conjugation of the ligand. The iminosemiquinone feature resembles that found for the monoligand, U(IV) complex $(^{dipp}isq)UI_3(THF)_2$, located at 763 nm (~650 M^{-1} cm^{-1}).[47] Chadhuri and Wieghardt have also reported a similar spectroscopic feature in Ni(II), Cu(II), and Pd(II) complexes with iminosemiquinone ligands, ranging from 750 to 900 nm.[48] The near-infrared region of the spectrum contains bands with low molar absorptivities indicative of an f^2 uranium(IV) center, confirming the proposed oxidation state of **6**. These bands are broad in comparison to complexes **4** and **5**, but consistent with the broadness in the absorption spectrum for $(^{dipp}ap)_2U(THF)_2$ (Figure 2).

The scope of oxidative addition was evaluated by variation of the halogen from Cl_2 to I_2 (eq 3). Dropwise addition of a THF solution of elemental iodine to **1** results in a color change to dark brown. Analysis of the isolated brown solid, **7**, by ^1H NMR spectroscopy (Figure S5) shows similar spectroscopic features to **4**, indicating the formation of the diiodide species. The structure of **7** was investigated by X-ray crystallography, confirming the formation of the monomeric $(^{tBu}isq)_2UI_2(THF)$ (**7**), with a seven coordinate uranium (Figure S6, Table S1). Because of the data quality, the oxidation state of the ligand was not elucidated based on intraligand distances alone. However, the U−N (2.514(12) and 2.567(14) Å) and U−O (2.160(10) and 2.164(10) Å) distances compare favorably to those of **5**, supporting ligand oxidation to form the iminosemiquinone derivative, $(^{tBu}isq)_2UI_2(THF)$. Electronic absorption spectroscopy from 280 to 2100 nm in THF at ambient temperature revealed sharp f−f transitions in the near-infrared region of the spectrum indicating a tetravalent uranium center,[38] with a band at 712 nm (976 M^{-1} cm^{-1}) corresponding to the $[^{R}isq]^{1-}$ ligand (Figure S7).

While similar observations have been noted following the addition of I_2 to complexes **2** and **3**, characterization of the bis(iminosemiquinone) products, $(^{R}isq)_2UI_2(THF)$ (R = Ad, dipp) has been challenging. Addition of iodine to an equivalent of either **2** or **3** results in the expected color changes to dark brown signifying the formation of the desired bis(iminosemiquinone) uranium diiodides, as observed in the case of **1**. However, following workup and recrystallization, decomposition was evident in the ^{1}H NMR spectra, which showed predominantly free ligand.

■ CONCLUSIONS

A family of uranium(IV) bis(amidophenolate) complexes, $({}^{R}ap)_2U(THF)_2$, was synthesized by salt metathesis of the potassium or sodium salt of the dianonic ligand with UCl_4. Characterization by ^{1}H NMR and electronic absorption spectroscopies support the tetravalent oxidation state of uranium and the absence of redox chemistry upon ligation to uranium. In the case of compounds **2** and **3**, X-ray crystallography confirmed the presence of two dianionic amidophenolate ligands per uranium center, and provided structural details for the geometric isomers of **2**. Additionally, the synthesis, characterization, and metalation of the adamantyl derivatized amidophenolate ligand have been presented, adding an electron-rich, sterically bulky member to the family of uranium amidophenolate species. Oxidative addition was observed upon addition of X_2 to a solution of $({}^{R}ap)_2U(THF)_2$, forming the "oxidized" species, $({}^{R}isq)_2UX_2$. The electronic absorption spectra show tetravalent uranium species supported by iminosemiquinone ligands, which is evident by bands between 700 and 800 nm, characteristic for the transition of the open-shell, iminosemiquinone ligand. This is further supported by crystallographic analyses, which show the expected bond distortions for a radical ligand. Thus, the bis(amidophenolate) ligand framework facilitates oxidative addition of halogens to a single uranium center by providing the reducing equivalents required to break the X−X bond (X = Cl, I). Given that uranium(VI) is an available oxidation state, it is significant that the redox chemistry that accompanies oxidative addition occurs at the ligand rather than the metal center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra, characterization for **7**, crystallographic experimentals, and cifs. 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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