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Uranium(III)/(IV) Nitrile Adducts Including $UI_4(N{\equiv}CPh)_4$, a Synthetically Useful Uranium(IV) Complex

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The synthesis of complexes used to elucidate an understanding of fundamental An(III) and An(IV) coordination chemistry requires the development of suitable organic-soluble precursors. The reaction of oxide-free uranium metal turnings with 1.3 equivalents of elemental iodine in acetonitrile provided the U(III)/U(IV) complex salt, $[U(N{\equiv}CMe)_9][UI_6][I]$ (**1**), in which the U(III) cation is surrounded by nine acetonitrile molecules in a tricapped trigonal prismatic arrangement, a $[UI_6]^{2-}$ counterion, and a noncoordinating iodide. The U–N distances for the prismatic and capping nitrogens are 2.55(3) and 2.71(5) Å, respectively. The same reaction performed in benzonitrile afforded crystalline $UI_4(N{\equiv}CPh)_4$ (**3**) in 78% isolated yield. In the solid state, **3** shows an eight-coordinate U(IV) atom in a “puckered” square antiprismatic geometry with U–N and U–I distances of 2.56(1) and 3.027(1) Å, respectively. This benzonitrile UI_4 adduct is a versatile U(IV) synthon that is soluble in methylene chloride, benzonitrile, and tetrahydrofuran, and moderately soluble in toluene and benzene, but decomposes in benzonitrile at 198 °C to $[UI(N{\equiv}CPh)_8][UI]_6$ (**4**), a U(III)/U(IV) salt analogous to **1**. A toluene slurry of **3** treated with 2.2 equiv of Cp*MgCl·THF (Cp* = pentamethylcyclopentadienide) provided $Cp^*_2UI_2(N{\equiv}CPh)$ (**5**) in low yields. Single-crystal X-ray structure determination shows that the iodide ligands in **5** are in a rare cis configuration with an acute I–U–I angle of 83.16(7)°. Treatment of a methylene chloride solution of **3** with KTp* (Tp* = hydridotris(3,5-dimethylpyrazolylborate)) formed green Tp^*UI_3 (**6**) which was converted to yellow $Tp^*UI_3(N{\equiv}CMe)$ (**7**) by rinsing with acetonitrile. Addition of 2.2 equiv of KTp* to a toluene solution of **3** followed by heating at 95 °C, filtration, and crystallization led to the isolation of the dinuclear species $[Tp^*UI(dmpz)]_2[\mu\text{-}O]$ (**9**) (dmpz = 3,5-dimethylpyrazolide), presumably formed by hydrolytic cleavage of excess KTp* by adventitious water. The Tp* complexes **6**, **7**, and **9** were characterized by single-crystal X-ray diffraction, NMR, FT-IR, and optical absorbance spectroscopies.

Introduction

We are studying low-valent early actinide (U−Cm) complexes with the goals of enhancing our understanding of fundamental An(III) and An(IV) coordination chemistry and supporting the development of selective separation agents. These efforts require a range of starting materials with varying chemical and physical properties that will allow us, for example, to prepare and structurally characterize model complexes of operative species involved in actinide/lanthanide separations. The synthesis of such compounds is, in many cases, hindered by the paucity of suitable precursors.

The anhydrous trivalent and tetravalent actinide halides are important starting materials that are commonly prepared by oxidation of the actinide metal with molecular halides. The anhydrous polymeric uranium trihalides are insoluble in common organic solvents.[1,2] Karraker has prepared slightly more soluble $AnI_3(THF)_x$ (An = Pu, Np) by treatment of actinide metals in THF suspensions with 1,2-diiodoethane but noted that uranium was unreactive toward $C_2H_4I_2$.[3] The more utilized An(III) reagents have been prepared through oxidation of An metal turnings (An = Np, Pu, and mercury-coated U) by iodine in polar aprotic solvents to form $AnI_3(sol)_4$ (sol = THF, py, or ½ dme).[4] We recently reported an

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alternative to actinide metal oxidation with molecular halides by using metal hexafluorophosphate salts as the oxidizing agent. For example, plutonium metal suspended in acetonitrile is oxidized to the homoleptic acetonitrile complex $[Pu(N{\equiv}CMe)_9][PF_6]_3$ in the presence of either silver or thallium hexafluorophosphate.[5] Acetonitrile solutions of these hexafluorophosphate salts will not oxidize uranium metal in the same fashion as plutonium; however, access to an analogous uranium triiodide, $[U(N{\equiv}CMe)_9][I]_3$, is achieved by dissolution of purple $UI_3(THF)_4$ in acetonitrile.[5] In contrast to the green $[U(N{\equiv}CMe)_9][I]_3$ product, direct oxidation of uranium metal by iodine in acetonitrile has been reported to give a dark brown crystalline material formulated as either $UI_4(N{\equiv}CMe)_4$[6] or $UI_3(N{\equiv}CMe)_4$,[7] depending on the amount of iodine used for the oxidation.

The preparation of the tetrahalide uranium species UI_4[2,8−11] and UBr_4[8,9] is laborious and tedious. Once UI_4 is prepared, it is unstable at room temperature and decomposes to uranium triiodide and iodine.[6,8,11,12] Iodine oxidation of uranium metal suspended in a dichlormethane benzophenone solution forms a putative $UI_4(O{=}CPh_2)_2$ intermediate that can be converted to $UI_4(N{\equiv}CMe)_4$ upon dissolution in acetonitrile in low yields; although neither of these products has been characterized by single-crystal X-ray diffraction, their structural assignments have been assigned using FT-IR and optical-absorbance spectroscopies.[6,12] In a recent contribution, Berthet and co-workers were able to access "$UI_4(N{\equiv}CMe)_4$" in high yields through metathesis of UCl_4 in acetonitrile using excess Me_3SiI. However, crystallization of the $UI_4(N{\equiv}CMe)_4$ product yields the $[UI_2(N{\equiv}CMe)_7][UI_6]$ salt as the structurally characterized product.[13]

Uranium tetrachloride is the most common precursor for the preparation of anhydrous uranium(IV) compounds. Even though UCl_4 can be prepared from the direct reaction of chlorine gas with uranium metal, it is more conveniently prepared by reducing uranium oxide in the chlorinating solvent hexachloropropene. The reaction proceeds under relatively harsh conditions (190 °C) and forms HCl and phosgene as products.[14−16] In this contribution, we report the facile preparation of a stable uranium tetraiodide complex, $UI_4(N{\equiv}CPh)_4$, in multigram quantities from the room-temperature oxidation of uranium metal by iodine in benzonitrile solvent. During our investigations, we revisited the analogous reactivity in acetonitrile solvent and were able to isolate and structurally characterize a mixed-valence U(III)/U(IV) product, $[U(N{\equiv}CMe)_9][I][UI_6]$, which has properties similar to those of the trivalent compound $UI_3(N{\equiv}CMe)_4$, previously reported.[7] A comparable mixed-valence adduct, $[UI(N{\equiv}CPh)_8][UI_6]$, was isolated in low yield by refluxing the crude reaction mixture of uranium oxidation by iodine in benzonitrile. The synthetic utility of $UI_4(N{\equiv}CPh)_4$ was investigated by treating this UX_4 synthon with Cp*MgCl·THF and KTp* under a variety of reaction conditions. The products from these reactions are described herein.

Experimental Section

General Comments. Oxide-free uranium turnings depleted in ^{235}U were prepared in a fashion similar to that of Sattelberger and co-workers;[17] however, ongoing efforts to minimize mixed radioactive hazardous waste disfavor the use of HgI_2 to prepare the mercury amalgamated uranium turnings described in their work. We prepared oxide-free turnings in the following manner: 10 g of oxide-coated U turnings were cut into 1-in. strips and then immersed in 100 mL of concentrated nitric acid to remove the oxide coating. The turnings remained in the acid until removal of the black oxide layer from the metal visibly stopped, and then they were transferred to a beaker containing 100 mL of fresh concentrated nitric acid. This nitric acid rinsing process was repeated three or more times to produce shiny metallic strips. Residual acid was removed by rinsing the turnings with deionized water, and residual water was removed by rinsing with copious amounts of dry THF. The turnings were then transferred into the drybox antechamber where residual THF was removed in vacuo; the metal was then used immediately. ***Safety Note:*** *Depleted uranium and its decay products are radioactive. Uranium and other radioactive materials should be handled only by trained and qualified workers in facilities equipped with appropriate controls*.

Hexanes, toluene, ether, and tetrahydrofuran solvents were dried by using activated alumina columns (A2, 12 × 32, Purify).[18,19] Anhydrous acetonitrile and benzonitrile were purchased from Aldrich, distilled from CaH_2, and stored over a 1:1 mixture of 3 and 4 Å molecular sieve pellets. All other solvents were purchased as anhydrous grades from Aldrich and stored over a 1:1 mixture of 3 and 4 Å molecular sieve pellets prior to use. Unless otherwise noted, all reactions were performed in either a Vacuum Atmospheres model HE-553-2 inert atmosphere drybox with a MO-40-2 Dri-Train or an MBraun Labmaster 130 drybox under a He or N_2 atmosphere. Infrared spectra were obtained on a Nicolet Magna-IR 560 spectrometer equipped with a DTGS detector. Thin film and Fluorolube mull IR spectra were obtained on CaF_2 plates. The Raman spectrum of $UI_4(N{\equiv}CPh)_4$ was obtained with CH_2Cl_2 solution sealed in a 5 mm NMR tube by exciting from an Ar^+ laser (Spectra Physics, model 2025) using the 514.5 nm line. The scattered light was dispersed and analyzed on a SPEX model 1403

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scanning double monochromator equipped with a 1800 groove/mm grating and a single-photon-counting detection system. Scan parameters were as follows: 1 cm^{-1} increments between points, integration for 3 s at each point, 71 scans averaged for the final spectrum, and a spectral resolution of 5 cm^{-1}. An external standard of Tylenol was used for energy calibration. Optical absorbance spectra were obtained in airtight, Teflon-capped, 1 cm quartz cuvettes on either a Varian Cary 6000i or a Varian Cary 500 UV−vis near-IR spectrophotometer. All ^{1}H, ^{13}C, and ^{11}B NMR samples were prepared in 4 mm Teflon NMR tube liners that were inserted into 5 mm NMR tubes to multiply contain the radioactive samples. Spectra were obtained at room temperature on a Bruker Avance 300 MHz spectrometer equipped with a Bruker broadband probe. The ^{1}H and ^{13}C spectra were referenced to the residual solvent resonances, and ^{11}B spectra were referenced to a $BF_3{\cdot}Et_2O$ external standard. The $[U(N{\equiv}CMe)_9][I]_3$,[5] KTp*,[20] and Cp*MgCl·THF[21] complexes were prepared using published procedures. Elemental and mass spectral analyses were performed by the Mass Spectrometry and Micro-Mass group at the University of California at Berkeley, Berkeley, CA.

$[U(N{\equiv}CMe)_9][UI_6][I]$ (1). Uranium turnings (0.102 g, 0.428 mmol) were added to a vial containing a magnetic stirbar and 4 mL of acetonitrile. A 4 mL suspension of iodine (0.149 g, 0.587 mmol) in acetonitrile was added to the vial containing the uranium, and then the red solution was stirred overnight. Filtration of the resulting turbid orange solution through a Whatman syringe filter provided a dark orange filtrate that was placed in a freezer overnight. The resulting large brown crystals (0.154 g, 50% isolated yield based on iodine) were determined to be $[U(N{\equiv}CMe)_9][UI_6][I]$ by single-crystal X-ray crystallography. UV−vis−NIR (MeCN): λ (nm) 557, 649, 776, 925, 1115, 1264.

$UI_4(N{\equiv}CPh)_4$ (3). Uranium turnings (2.08 g, 8.74 mmol) were added to a 250 mL Erlenmeyer flask containing a stirbar and 40 mL of benzonitrile. This suspension was stirred as iodine (2.66 g, 10.5 mmol) was added over 5 min. Within 20 min after the addition of iodine, the color of the suspension changed to dark orange/black. A red precipitate formed as this suspension was stirred overnight. Filtration through a coarse porosity glass fritted funnel provided a small amount of red microcrystalline material, unreacted U, and a red filtrate. The unreacted U was manually separated from the red crystalline material and reclaimed for later use. A 100 mL portion of hexanes was added to the red filtrate, and a red microcrystalline material precipitated. Isolation of the microcrystalline material by filtration, rinsing with three 20 mL portions of hexane, and removal of residual solvent in vacuo provided 4.514 g (74% yield based on iodine) of analytically pure red $UI_4(N{\equiv}CPh)_4$. Crystals suitable for X-ray crystallography were obtained from a saturated benzonitrile solution that was gently heated, filtered, and cooled to room temperature. ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.44 (t, $^{3}J_{HH} = 7.0$ Hz, 4 H_{para}), 4.22 (br s, 8 H_{meta}), 0.80 (br s, 8 H_{ortho}). Raman: ν_{NC} 2250 cm^{-1} (CH_2Cl_2). UV−vis−NIR (CH_2Cl_2): λ (nm) (ϵ, $M^{-1}{\cdot}cm^{-1}$) 690 (140), 825 (23), 877 (22), 962 (25), 1051 (43), 1165 (130). IR: ν_{NC} 2254 cm^{-1} (thin film from CH_2Cl_2 solution evaporation on CaF_2 plates). Anal. Calcd for $C_{28}H_{20}I_4N_4U$: C, 29.04; H, 1.74; N, 4.84. Found: C, 29.08; H, 1.71; N, 4.70.

$[UI(N{\equiv}CPh)_8][UI_6]$ (4). Iodine (9.16 g, 36.1 mmol) was added to a 500 mL Schlenk flask containing uranium turnings (6.70 g, 28.15 mmol), 200 mL of benzonitrile, and a stirbar. The flask was capped with a ground-glass stopper, removed from the drybox, and connected to a nitrogen-flushed reflux condenser attached to a Schlenk line. The dark red solution was stirred at room temperature under continuous nitrogen flow for 12 h and then heated to reflux for 5 min. This hot reaction flask was then transferred to the drybox, and the contents were filtered through a 30-mL coarse porosity glass fritted funnel. Unreacted U metal and a black microcrystalline solid were collected. Manual separation of the uranium followed by rinsing the black solid with 50 mL of toluene and removal of residual solvent in vacuo provided 5.39 g of crystalline material determined to be $[UI(N{\equiv}CPh)_8][UI_6]$ (2.46 mmol, 18% yield based on uranium) by single-crystal X-ray diffraction. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.82 (br, s, 8 H_{para}), 8.15 (br s, 16 H_{ortho}), 7.01 (br s, 16 H_{meta}). UV−vis−NIR (CH_2Cl_2): λ (nm) 683, 925, 1052, 1159, 1256. Anal. Calcd for $C_{56}H_{40}I_7N_8U_2$: C, 30.72; H, 1.84; N, 5.12. Found: C, 30.0; H, 1.65; N, 4.64.

$Cp^*_2UI_2(N{\equiv}CPh)$ (5). A 100 mL Schlenk tube was charged with **3** (2.0 g, 1.72 mmol), Cp*MgCl·THF (1.07 g, 4.0 mmol), 50 mL of toluene, and a stirbar. The tube was sealed, removed from the drybox, immersed in a 95 °C oil bath, and heated for 15 h. The flask was returned to the drybox, and the solution was filtered to remove an uncharacterized gray solid that was rinsed with toluene. The resulting dark red/orange filtrate was then twice passed through Celite-545 padded coarse glass fritted funnels, and the volume was reduced to ∼25 mL in vacuo. This dark red solution was triturated with 25 mL of hexane, stirred for 24 h, and filtered twice through a Celite-545 padded coarse fritted funnel to remove the fine white precipitate (presumably Mg salts) that formed. The collected red filtrate was placed in a freezer at −35 °C, and the dark brown crystals that formed within 24 h were collected and determined by single-crystal X-ray crystallography to be $Cp^*_2UI_2(N{\equiv}CPh)$ (0.535 g, 36% yield). ^{1}H NMR (0.3 mL PhCN/0.1 mL CD_2Cl_2 solution): δ (ppm) 14.00 (30 Cp* H). MS: $[M - C_7H_5N]^+$ 762. Anal. Calcd for $C_{27}H_{35}I_2NU$: C, 37.47; H, 4.08; N, 1.62. Found: C, 39.62; H, 4.39; N, 1.67.

Tp^*UI_3 (6). A 50 mL sidearm flask was charged with **3** (1.35 g, 1.17 mmol), 20 mL of CH_2Cl_2, and a magnetic stirbar. The resulting red solution was stirred as KTp* (0.485 g, 1.44 mmol) was added in 3 portions over a period of 5 min. After 1 h of stirring, the solution color gradually turned green-yellow and was filtered through a Celite 545 padded coarse glass fritted funnel. The filter plug was washed with 20 mL of dichloromethane, and the green filtrate was isolated. Removal of solvent from the filtrate in vacuo yielded a green solid that was rinsed with toluene, benzene, or ether. Residual solvent was removed in vacuo, and a bright green Tp^*UI_3 solid (0.652 g, 61% yield) was isolated. Green-yellow crystals were obtained as $Tp^*UI_3{\cdot}(toluene)_3$ by cooling a saturated toluene solution of Tp^*UI_3 to −38 °C. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.80 (s, 3 Tp* C−*H*), 5.49 (s, 9 Tp* C*H*$_3$), −7.71 (s, 9 C*H*$_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 164.4 (s, Tp* *C*−CH_3), 136.5 (d, $^{1}J_{CH} = 177.4$ Hz, Tp* *C*−H), 134.8 (s, Tp* *C*−CH_3), 20.16 (q, $^{1}J_{CH} = 129.8$ Hz, Tp* C−*C*H_3), −0.31 (q, $^{1}J_{CH} = 129.8$ Hz, Tp* C−*C*H_3). ^{11}B NMR (CD_2Cl_2): δ (ppm) 21.97 (d, $^{1}J_{H} = 141$ Hz, Tp* −H). UV−vis−NIR (CH_2Cl_2): λ (nm) (ϵ, $M^{-1}{\cdot}cm^{-1}$) 498 (46), 599 (17), 632 (11), 658 (73), 677 (82), 747 (10), 783 (10), 815 (10), 910 (14), 959 (13), 999 (10), 1114 (46), 1131 (42), 1164 (12), 1266 (16). MS: M^+ 916. IR (Fluorolube mull): ν_H 1538 cm^{-1}. Anal. Calcd for $C_{17}H_{25}N_6I_3U$: C, 21.34; H, 2.63; N, 10.25. Found: C, 21.27; H, 2.31; N, 10.34.

$Tp^*UI_3(N{\equiv}CMe)$ (7). Rinsing either crude **6** after filtration through Celite or pure **6** with MeCN results in quantitative conversion to golden brown $Tp^*UI_3(N{\equiv}CMe)$. Crystals were obtained from vapor diffusion of hexane into a CH_2Cl_2 solution of $Tp^*UI_3(N{\equiv}CMe)$. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.81 (s, 3 Tp*

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Table 1. Crystallographic Parameters for Complexes **1**, **3**−**7**, and **9**

complex	**1**	**3**	**4**	**5**	**6**	**7**	**9**
empirical formula	$C_{18}H_{27}I_7N_9U_2$	$C_{112}H_{80}I_{16}N_{16}U_4$	$C_{56}H_{40}I_7N_8U$	$C_{27}H_{35}I_2NU$	$C_{36}H_{46}I_3N_6U$	$C_{17}H_{25}I_3N_7U$	$C_{20}H_{29}IN_8O_{0.5}U$
fw	1733.85	4632.44	1951.29	865.39	1192.33	956.98	765.25
T (K)	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P\bar{6}c2$ (No. 188)	$I\bar{4}$	$P4/m$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	10.9169(19)	16.898(5)	12.221(3)	17.021(6)	17.943(9)	14.538(4)	18.520(4)
b (Å)	10.9169(19)	16.898(5)	12.221(3)	8.725(3)	18.658(9)	10.323(3)	11.972(3)
c (Å)	21.622(5)	11.615(3)	10.806(4)	19.189(7)	20.265(10)	17.448(5)	24.861(5)
α (deg)	90	90	90	90	90	90	90
β (deg)	90	90	90	104.294(6)	116.276(6)	99.301(5)	107.242(4)
γ (deg)	90	90	90	90	90	90	90
V (Å)^3	2231.6(8)	3316.6(16)	1613.8(9)	2761.3(17)	6083(5)	2584.0(13)	5264.5(18)
Z	2	1	1	4	8	4	8
ρ_{calcd} (g/cm^3)	2.580	2.319	2.008	2.082	2.604	2.460	1.931
μ (mm^{-1})	12.109	8.639	5.901	8.128	8.424	9.883	7.364
φ range (deg)	1.9−25.3	1.7−28.4	1.7−22.4	1.2−25.1	1.3−23.3	1.4−28.0	1.7−28.1
R^a	0.0694	0.0571	0.0811	0.0820	0.0606	0.0353	0.0672
$R_w{}^a$	0.2141	0.1429	0.1195	0.2522	0.0751	0.0852	0.1701

^{a} $R = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o{}^2) + (aP)^2]$.

C−*H*), 5.50 (s, 3 N≡CC*H*$_3$), 1.94 (s, 9 Tp* C*H*$_3$), −7.71 (s, 9 C*H*$_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 163.9 (s, Tp* *C*−CH_3), 135.93 (d, $^1J_{CH}$ = 177.3 Hz, Tp* *C*−H), 134.2 (s, Tp* *C*−CH_3), 19.66 (q, $^1J_{CH}$ = 129.8 Hz, Tp* C−*C*H_3), 1.71 ($^1J_{CH}$ = 135.8 Hz, N≡C*C*H_3), −0.89 (q, $^1J_{CH}$ = 129.8 Hz, Tp* C−*C*H_3). ^{11}B NMR (CD_2Cl_2): δ (ppm) 22.16 (d, ^1J_H = 89.5 Hz, Tp* −H). UV−vis−NIR (CH_2Cl_2): λ (nm) 700, 953, 1112. IR (Fluorolube mull): ν_H 1538 cm^{-1}, ν_{CN} 2269 cm^{-1}. Anal. Calcd for $C_{17}H_{25}N_7I_3U$: C, 21.34; H, 2.63; N, 10.25. Found: C, 21.27; H, 2.31; N, 10.34.

[Tp*]$_2$[UI$_6$] (8). Crystals of **8** were obtained by vapor diffusion of hexanes into a pyridine solution of Tp*UI_3(N≡CMe).

[Tp*UI(dmpz)]$_2$[μ-O] (9). A 100 mL Schlenk tube was charged with **3** (1.42 g, 0.986 mmol), KTp* (0.734 g, 2.18 mmol), 40 mL of toluene, and a stirbar and then heated at 95 °C, as in **5**, to produce a yellow-brown solution after 15 h. A tan solution and an uncharacterized brown solid were isolated after filtration through a coarse porosity glass fritted funnel. The brown solid was discarded, and the tan solution was filtered through a Celite padded coarse fritted funnel. The volume of collected grayish-yellow filtrate solution was reduced to 10 mL in vacuo, transferred to a scintillation vial, and stored in a −35 °C freezer for 1 month. Dull green crystals were isolated and assayed by single-crystal X-ray crystallography. Removal of solvent in vacuo provided analytically pure [Tp*UI(dmpz)]$_2$[μ-O] as a gray-green solid (0.688 g, 91% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 70.22, 20.12, −2.74, −8.09, −14.10, −18.06, −39.18 (3 H each from either Tp* C−C*H*$_3$ or dmpz C−C*H*$_3$). UV−vis−NIR (CH_2Cl_2): λ (nm) (ϵ) (M^{-1}·cm^{-1}) 476 (113), 512 (60), 662 (103), 688 (123), 943 (61), 1050 (138), 1115 (137), 1275 (55). Anal. Calcd for $C_{40}H_{582}I_2N_{16}OU_2$: C, 31.39; H, 3.82; N, 14.64. Found: C, 31.73; H, 4.01; N, 14.64.

The crystal structures of all compounds were determined as follows, with exceptions noted in subsequent paragraphs: A crystal was mounted onto a glass fiber using a spot of silicone grease. Because of air sensitivity, the crystal was mounted from a pool of mineral oil under argon gas flow. The crystal was placed on a Bruker P4/CCD diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The instrument was equipped with a sealed, graphite, monochromatized Mo Kα X-ray source (λ = 0.71073 Å). A hemisphere of data was collected using φ scans with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART[22] software. Frame integration, including Lorentz polarization corrections, and final cell parameter calculations were carried out using SAINT[23] software. The data were corrected for absorption using the SADABS[24] program. Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using Direct methods (SHELXS-97) and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom to which they were attached. The final refinement included anisotropic temperature factors on all non-hydrogen atoms (SHELXL-97). Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL 5.10.[25] Additional details of data collection and structure refinement are listed in Table 1.

Compound 1. Hydrogen atom positions were not modeled on the acetonitrile methyl carbon atom C2; this methyl group was disordered across a mirror plane. The anisotropic refinement of carbon atom C2 was constrained to approximate isotropic behavior. The structure was refined as a racemic twin, with the batch scale factor converging to 0.10(3). A lattice void of 92.00 Å^3 was observed in the unit cell, but because the residual electron density in the void was less than 2 e$^-$/Å^3, a disordered solvent molecule was not modeled.

Compound 3. The structure was refined as a racemic twin, with the batch scale factor converging to 0.46(1).

Compound 4. The molecule was disordered across a site of 4/*m* crystallographic symmetry, and all atomic positions were refined at one-half occupancy. Hydrogen atom positions were not modeled on the one-half occupancy phenyl groups. The phenyl groups were restrained to be rigid bodies.

Compound 6. The electron density of 24 disordered toluene molecules (299 e$^-$/cell and 1721 Å^3) was removed from the unit cell using PLATON/SQUEEZE.[26]

Results and Discussion

Oxidation of Uranium Metal with Iodine in Acetonitrile. We revisited the reactivity of uranium metal toward oxidation by iodine in acetonitrile solvent. Our attempts to isolate UI_3(N≡CMe)$_4$ from the oxidation of uranium metal by 1.3 equivalents of iodine in acetonitrile were not suc-

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(23) *SAINT-NT 5.050*; Bruker AXS, Inc.: Madison, WI, 1998.

(24) Sheldrick, G. M. *SADABS*, first release; University of Göttingen: Göttingen, Germany.

(25) *SHELXTL-NT*, version 5.10; Bruker AXS, Inc.: Madison, WI, 1997.

(26) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46 (supplement)*, C34.

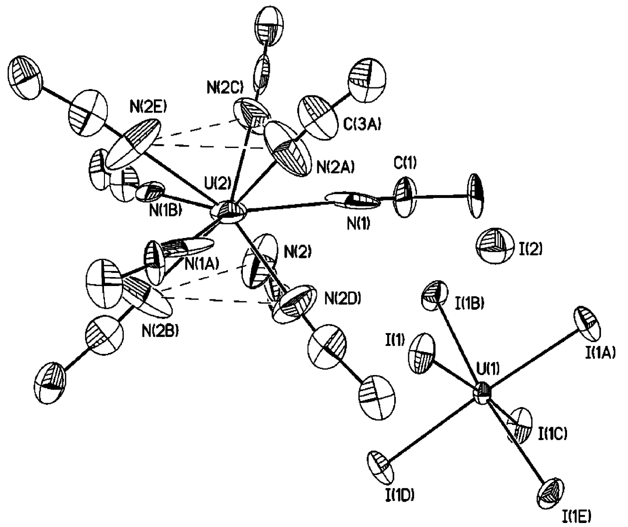

Figure 1. Thermal ellipsoid plot of $[U(N{\equiv}CMe)_9][UI_6][I]$ (**1**) at the 35% probability level. Selected bond lengths (Å): U(2)−N(1) = 2.71(5); U(2)−N(2) = 2.55(3); U(1)−I(1) = 2.987(1); U(2)−I(2) = 6.303(1); N(2)−C(3) = 1.16(4); N(1)−C(1) = 1.13(6). Selected bond angles (deg): N(1B)−U(2)−N(1A) = N(1A)−U(2)−N(1) = N(1)−U(2)−N(1B) = 120.000(5). The dashed lines are a visual aid showing the terminal faces of the trigonal prism.

cessful. Instead, we were able to isolate brown crystals of the mixed U(III)/U(IV) compound $[U(N{\equiv}CMe)_9][UI_6][I]$ (**1**) as the only product. The crystal structure of **1** (Figure 1) is a complex U(III)/U(IV) salt that contains a U(III) atom surrounded by nine acetonitrile solvent molecules. A noncoordinating $[UI_6]^{-2}$ anion and a noncoordinating iodide anion flank the symmetric U(III) nitrile adduct. The $[UI_6]^{-2}$ anion and the U(III) cation respectively occupy positions of D_3 and C_{3h} crystallographic site symmetry. The coordination geometry around the U(III) cation is an ideal tricapped trigonal prism with nine N-bound acetontrile molecules. The U(2)−N(2) distance of 2.55(3) Å for the prismatic nitrogens is 0.13 Å shorter than the U(2)−N(1) distance of 2.71(5) Å observed for the three capping nitrogens. These distances are within errors of the $U-N_{prismatic}$, 2.60(2) Å, and $U-N_{capping}$, 2.65(2) Å, distances reported for the cation in the compound $[U(N{\equiv}CMe)_9][I]_3$ (**2**).[5]

Complex **1** is insoluble in nonpolar organic solvents and CH_2Cl_2 and soluble in THF and acetonitrile. The ^1H NMR in THF-d_8 shows a single resonance for free acetonitrile, indicating complete displacement of bound acetonitrile by THF-d_8. The optical absorbance spectrum of an orange acetonitrile solution of $[U(N{\equiv}CMe)_9][UI_6][I]$ in the NIR region contains Laporte forbidden f → f bands.[4,27] The superimposed spectra of three trivalent uranium nitrile compounds are shown in Figure 2. The similarity of the complex **1** (green solution in acetonitrile) and complex **2** (orange solution in acetonitrile) spectra in the NIR region suggests that the optical transition arises from the $[U(N{\equiv}CMe)_9]^{3+}$ chromophore. These data, along with the solid-state structures for complexes **1** and **2**, underscore the poor U(III) coordinating ability of iodide in the presence of excess acetonitrile.

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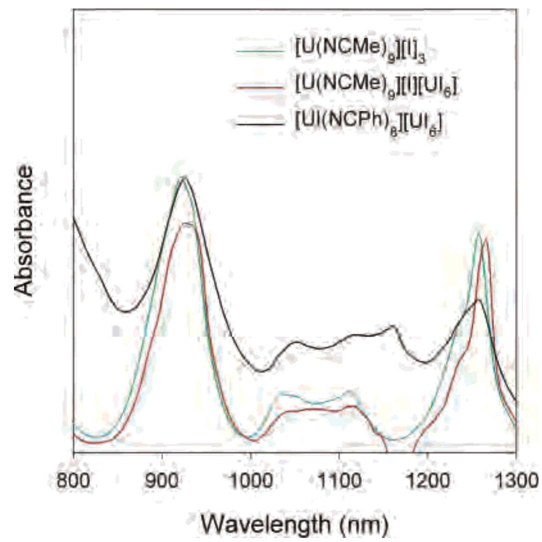

Figure 2. Superimposed NIR optical absorption spectra for complexes with a trivalent uranium cation containing bound nitrile ligands: $[U(N{\equiv}CMe)_9][UI_6][I]$ (**1**) in MeCN, $[U(N{\equiv}CMe)_9][I]_3$ (**2**) in MeCN, and $[UI(NCPh)_8][UI_6]$ (**4**) in CH_2Cl_2.

Oxidation of Uranium Metal with Iodine in Benzonitrile. Given the difficulty in preparing both UI_4 and UCl_4, alternative routes to obtaining uranium tetrahalides under mild conditions and in high yields would be synthetically useful. Other than UI_4, $UI_4(N{\equiv}CMe)_4$ is the only characterized tetraiodide uranium complex prepared from the oxidation of uranium metal. $UI_4(N{\equiv}CMe)_4$ can be prepared via direct oxidation in MeCN; however, multiple intractable products form, and the desired $UI_4(N{\equiv}CMe)_4$ product is difficult to isolate and is yet to be structurally characterized by X-ray crystallography.[6] If the iodine oxidation is performed in CH_2Cl_2 in the presence of benzophenone, then $UI_4(O{=}CPh_2)_2$ is isolated as the putative intermediate. The addition of MeCN followed by cooling to −18 °C ultimately affords $UI_4(N{\equiv}CMe)_4$ in an overall yield of 36%.[6,12] Unfortunately, $UI_4(N{\equiv}CMe)_4$ is insoluble in most useful organic solvents except THF, where it decomposes to a haloalkoxide product from ring opening of THF.[28] Similar reactivity is observed for UI_4.[29] Other uranium nitrile adducts of the type $UX_4(N{\equiv}C{-}R)_4$ (X = Cl or r; R = Me, Et, *n*-Pr, *n*-Bu, and Ph) have been prepared by dissolution of UX_4 into the appropriate nitrile.[30] The only structurally characterized $UX_4(nitrile)_x$ adduct prepared using this synthetic methodolgy is $UCl_4(N{\equiv}CMe)_4$.[31,32]

An excess of oxide-free uranium metal turnings suspended in benzonitrile reacts with iodine to yield microcrystalline, red $UI_4(N{\equiv}CPh)_4$ (**3**) in 74% isolated yield after overnight stirring. This compound is easily prepared on a synthetically useful 5-g scale, and the mild conditions are preferable to the high-temperature furnace techniques that yield UI_4 and

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(29) Collin, J.; Pires de Matos, A.; Santos, I. *J. Organomet. Chem.* **1993**, *463*, 103−107.
(30) Gans, P.; Marriage, J. *J. Chem. Soc., Dalton Trans.* **1972**, 46−48.
(31) Van den Bossche, G.; Rebizant, J.; Spirlet, M. R.; Goffart, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1478−1480.
(32) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 1186−1188.

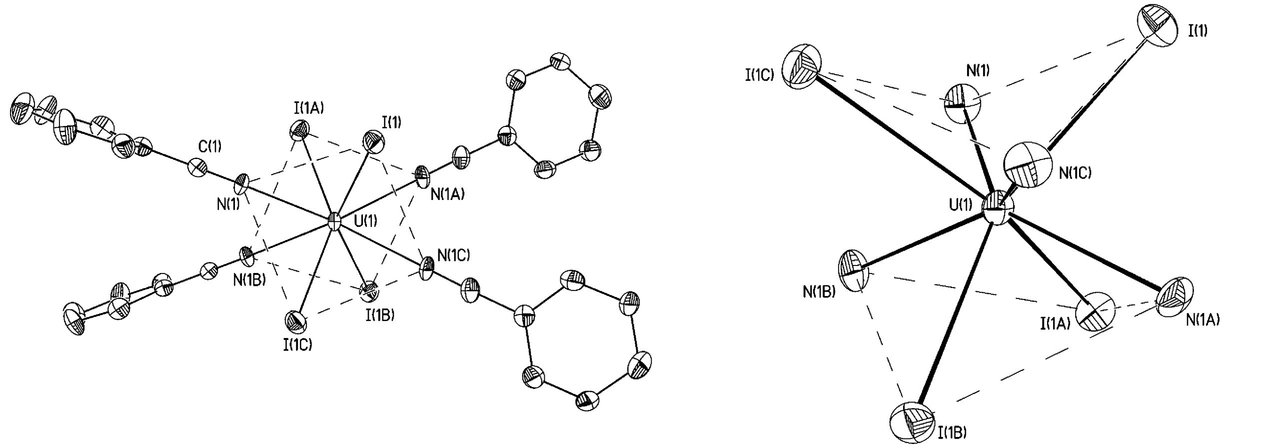

Figure 3. Thermal ellipsoid plot of $UI_4(N{\equiv}CPh)_4$ (**3**) at the 35% probability level (left) and the intimate coordination geometry about the central U(IV) atom (right). Selected bond lengths: (Å) U(1)−N(1) = 2.56(1); U(1)−I(1) = 3.027(1); N(1)−C(1) = 1.15(1). Selected bond angles (deg): I(1)−N(1)−I(1C) = 81.1(1). The dashed lines are a visual aid representing the puckered terminal faces of the distorted square antiprism.

the multistep synthesis that generates $UI_4(N{\equiv}CMe)_4$. Unlike UI_4, which decomposes via I_2 loss to UI_3 at room temperature, complex **3** is stable for months at room temperature in an inert atmosphere drybox. The air-sensitive compound is soluble in benzonitrile, CH_2Cl_2, and THF; moderately soluble in benzene and toluene; and insoluble in hexanes and ether. The structure of the $UI_4(N{\equiv}CPh)_4$ crystalline material was determined by single-crystal X-ray diffraction and is shown in Figure 3.

The crystal structure of **3** shows an eight-coordinate U(IV) atom in a "puckered" square antiprismatic geometry. The uranium atom is bound to one N atom from each of the four benzonitrile ligands and four iodides. The U−N and U−I distances are 2.56(1) and 3.027(1) Å, respectively. The planes of an ideal square antiprism defined by either I(1C)−N(1)−I(1)−N(1C) or I(1B)−N(1B)−I(1A)−N(1A) are puckered by a unique 81.1(1)° angle between each I(1)−N(1)−I(1). Complex **3** has S_4 molecular symmetry and is more symmetric than $UCl_4(N{\equiv}CMe)_4$ which has C_2 symmetry.[31,32]

The ^{1}H NMR of **3** in CD_2Cl_2 shows three paramagnetically broadened resonances at $\delta = 0.80$, 4.22, and 6.44 ppm for each of the ortho, meta, and para hydrogens, respectively, of the equivalent benzonitrile ligands coordinated to the U(IV) center. The resonance at 6.44 ppm is broad (~20 Hz); however, it appears as a triplet with $^3J_{HH} = 7$ Hz and is assigned as the resonance for the four equivalent para hydrogens of each benzonitrile ligand. The remaining two resonances integrate for eight hydrogens each. The broadest resonance (~45 Hz) at 0.80 ppm is assigned to the ortho hydrogens because they are closest to and most influenced by the paramagnetic U(IV) center; the next broadest resonance (~25 Hz) at 4.22 ppm is assigned to the meta hydrogens. The FT-IR spectrum of **3**, obtained as a thin film, shows an absorption band corresponding to the vibrational frequencies of bound nitriles at $\nu_{NC} = 2254$ cm^{-1}; the Raman spectrum in CH_2Cl_2 solution shows a similar band at $\nu_{NC} = 2250$ cm^{-1}. This ~25-cm^{-1} increase in the nitrile C≡N stretching frequency (compared to $\nu_{NC} = 2228$ cm^{-1} for free benzonitrile) is expected after coordination of the nitrile nitrogen to the electropositive U(IV) center and is similar

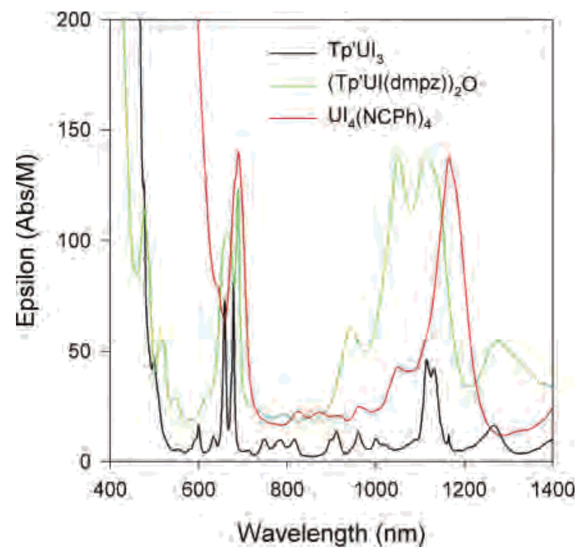

Figure 4. Optical absorption spectra of $UI_4(N{\equiv}CPh)_4$ (**3**), Tp^*UI_3 (**6**), and $[Tp^*UI(dmpz)]_2[\mu\text{-}O]$ (**9**) in CH_2Cl_2 solutions.

to the 28-cm^{-1} increase in ν_{NC} observed for acetonitrile coordination to UCl_4.[33]

The UV−vis−NIR spectrum of complex **3** dissolved in methylene chloride is shown in Figure 4. The absorption maxima at 690 and 1165 nm are typical for U(IV) observed in 1 M perchloric acid (deuterated) solution[27] and also agree favorably with absorption maxima of structurally characterized U(IV) iodide coordination complexes derived from $UI_4(N{\equiv}CPh)_4$ dissolved in methylene chloride (vide infra). A cyclic voltammogram of **3** in the noncoordinating ionic liquid 2-ethyl-5-methylimidazolium bis(trifloumethanesulfon)imide shows a reduction wave at −0.40 V (vs silver wire). The reoxidation wave is not observed, indicating that the U(III) complex is unstable in the ionic liquid.

During one preparation of **3**, we attempted to dissolve the crude $UI_4(N{\equiv}CPh)_4$ product by heating the benzonitrile suspension to reflux. After 5 min at 191 °C, the red $UI_4(N{\equiv}CPh)_4$ precipitate disappeared and a black precipitate formed. Filtration of this solution resulted in the isolation

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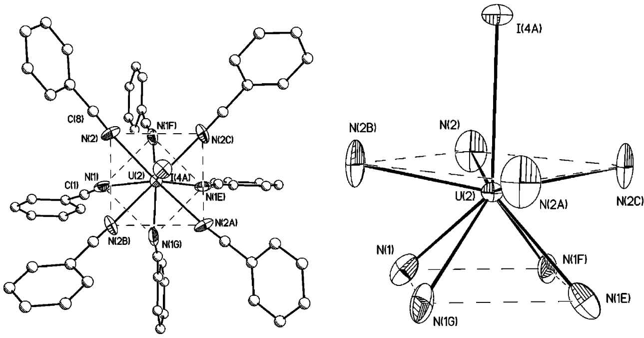


Figure 5. Structure of the $[UI(N{\equiv}CPh)_8]^{2+}$ cation in **4** (left) with thermal ellipsoids at the 35% probability level shown for the N, U, and I atoms, and the intimate coordination geometry about the central U(III) atom (right). Selected bond lengths (Å): U(2)−N(1) = 2.64(1); U(2)−N(2) = 2.54(1); U(2)−I(4) = 3.209(3); $[N2-N(2A)-N(2B)-N(2C)]_{centroid}-U(2)$ = 0.05(1) Å; $[N1-N(1E)-N(1F)-N(1G)]_{centroid}-U(2)$ = 1.70(1) Å. Selected bond angles (deg): I(4)−U(2)−N(2) = 78.62(5); N(1)−U(2)−I(4) = 130.4(3). The dashed lines are a visual aid representing the terminal faces of the square antiprism.

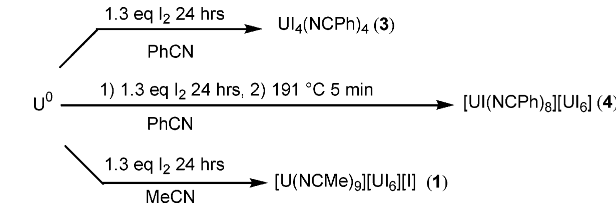
of a black microcrystalline material, determined by single-crystal X-ray crystallography to be $[UI(N{\equiv}CPh)_8][UI_6]$ (**4**) in 18% yield and likely formed by thermally induced iodide loss from **3**. This decomposition suggests that, although complex **3** is much more stable than UI_4, $UI_4(N{\equiv}CPh)_4$ decomposes through a pathway similar to that observed for UI_4. The structure of the cation in the mixed U(III)/U(IV) salt $[UI(N{\equiv}CPh)_8][UI_6]$ is shown in Figure 5.

The thermal ellipsoid plot of **4** shows a nine-coordinate U(III) complex ion and a noncoordinating $[UI_6]^{-2}$ counterion. The central uranium atom in the cation adopts a highly distorted monocapped square antiprismatic geometry where eight N atoms of the coordinating benzonitrile molecules form the square antiprism, with iodide as the capping ligand. The U(III) and U(IV) ions occupy positions of C_{4h} and 4-fold crystallographic symmetry, respectively. The central U(III) atom is nine-coordinate, as observed in the U(III) iodide organonitrile species **1** and **2**. However, in this case, an iodide ligand is situated in the pocket formed by the four benzonitrile molecules that form the square antiprism face instead of in the one formed by nine N-bound nitriles and all outer sphere iodides. If the square antiprismatic portion of the U(III) cation is considered, then the distortion arises from the position of the central U(III) atom with respect to the centroids of the square planes that form the terminal faces of the antiprism. In fact, the uranium atom is almost coplanar with all four N(2) atoms and sits only 0.05(1) Å below the centroid of the N(2)−N(2A)−N(2B)−N(2C) plane as compared to the 1.70(1) Å above the centroid of the plane defined by the four N(1) atoms.

Complex **4** is insoluble in the nonpolar solvents toluene, ether, and hexane but is soluble in methylene chloride. The optical absorbance spectrum of a brown methylene chloride solution of **4** is similar to those for the homoleptic U(III) acetonitrile adducts, as shown in Figure 1, confirming the presence of U(III).

The ^{1}H NMR spectrum of **4** in CD_2Cl_2 shows three paramagnetically broadened resonances at δ = 8.82, 8.15, and 7.01 ppm in a 1:2:2 ratio. The broadest resonance (~80 Hz) at 8.15 ppm is assigned to the ortho hydrogens that are closest to and most influenced by the paramagnetic U(III) center. The remaining two signals at 7.01 and 8.82 ppm are equally broad (~30 Hz) and correspond to meta and para hydrogens, respectively, but the upfield resonance at 7.01 ppm is twice as intense as the downfield resonance at 8.82 ppm. The simplicity of the ^{1}H NMR spectrum may arise from the weak coordinating ability of iodide toward U(III) in solution.[5,34] Iodide likely dissociates from $[UI(N{\equiv}CPh)_8]^+$ to form an ion paired $[U(N{\equiv}CPh)_8]^{2+}$ cation that is symmetric on the NMR time scale. An overall scheme of the products obtained by uranium oxidation by iodine in nitrile solvents is shown in Scheme 1.

Scheme 1. Oxidation of Uranium Metal by Iodine in Nitrile Solvents[a]



[a] Equations are not balanced and reflect the reaction conditions used to prepare each uranium nitrile adduct.

Reactivity of $UI_4(N{\equiv}CPh)_4$. A. Addition of Cp*MgCl·THF. Uranium(IV) bis-metallocene chemistry is dominated by the $Cp^*{}_2UCl_2$ (Cp* = pentamethylcyclopentadienide) starting material[21,35−37] because of its ready preparation from UCl_4 and Cp*MgCl·THF. The lack of a useful UI_4-type starting material presumably has precluded isolation of the analogous $Cp^*{}_2UI_2$ compound, which has been characterized spectroscopically as a product from the in situ oxidative addition reactions of $Cp^*{}_2UCl$·THF with either iodine or alkyl iodides and by iodide transfer from I_3 to $Cp^*{}_2UCl_2$.[38] We attempted the preparation of $Cp^*{}_2UI_2$ by treating **3** with Cp* reagents.

Addition of 2.4 equiv of Cp*MgCl·THF to a slurry of **3** in toluene, followed by overnight heating, leads to the isolation of $Cp^*{}_2UI_2(N{\equiv}CPh)$ (**5**) in 36% isolated yield. Unfortunately, treatment of **3** with excess KCp* under identical conditions yielded intractable products. The crystal structure of **5**, shown in Figure 6, is of the Cp_2MX_2Y type, with uranium coordinated by two pentamethylcyclopentadienides, two iodides, and the nitrogen of benzonitrile. This is an uncommon coordination geometry for $Cp^*{}_2U$ compounds, with the most similar being $Cp^*{}_2UCl_2(L)$ (L = HN=PPh_3,[39] HN=SPh_2,[40] and pyrazole[41]). However, unlike the latter compounds where the N-donor ligand binds to the

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(39) Cramer, R. E.; Roth, S.; Gilje, J. W. *Organometallics* **1989**, *8*, 2327−2330.

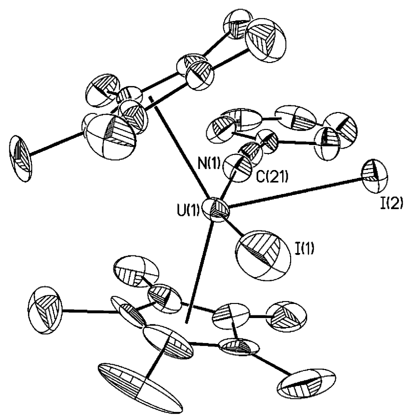

Figure 6. Thermal ellipsoid plot of $Cp^*_2UI_2(N{\equiv}CPh)$ (**5**) at the 35% probability level. Selected bond lengths (Å): U(1)−Cp*(centroid) = 2.48(2) and 2.45(2); U(1)−N(1) = 2.53(1); U(1)−I(1) = 2.942(3); U(1)−I(2) = 3.092(2); N(1)−C(2) = 1.14(2). Selected bond angles (deg): Cp*(centroid)−U(1)−Cp*(centroid) = 136.7(5); N(1)−U(1)−I(2) = 70.6(4); N(1)−U(1)−I(1) = 153.8(4); I(2)−U(1)−I(1) = 83.16(7).

uranium center inside the ~150° Cl−U−Cl "wedge" formed by the chlorides, the iodides in **5** are cis to each other, forming an acute I−U−I angle of 83.16(7)°. In fact, the acute I−U−I angle is almost 15° smaller than the 97.9° Cl−U−Cl angle in $Cp^*_2UCl_2$.[42]

The two U−Cp* centroid distances of 2.45(2) and 2.48(2) Å and the Cp*(centroid)−U−Cp*(centroid) angle of 136.7(5)° are similar to known Cp*An complexes, and the Cp* rings are arranged in the sterically favored staggered arrangement. The three atoms in the equatorial positions are in the same plane because the sum of the N(1)−U(1)−I(2) and I(2)−U(1)−I(1) angles, 70.6(4) and 83.16(7)°, respectively, equals the 153.8(4)° N(1)−U(1)−I(1) angle. The U(1)−N(1) bond length of 2.53(1) Å is similar to the U−N bond length observed in $UI_4(N{\equiv}CPh)_4$. There are two U−I distances in **5**, 2.942(3) and 3.092(2) Å, which are 0.3−0.4 Å longer than the U−Cl bonds in the analogous $Cp^*_2UCl_2$(L) complexes but similar to the 2.954 Å lengths reported for Cp'_2UI_2 (Cp′ = 1,3-bis(trimethylsilyl)cyclopentadienide), the only structurally characterized bis(cyclopentadienido) uranium diiodide reported;[43] the U−I distances in $UI_4(N{\equiv}CPh)_4$; and the $[UI_6]^{-2}$ counterions observed in the mixed-valent U(III)/U(IV) nitrile compounds (vide supra).

The ^1H NMR spectrum of complex **5** in C_6D_6 displays resonances at 18.0 and 15.6 ppm in approximately a 2:1 ratio and displays benzonitrile resonances between 6.8 and 6.5 ppm. Addition of a single drop of benzonitile to the sample results in the disappearance of the 15.6 ppm resonance and the appearance of a 14.2 ppm resonance. The intensities of the 18.0 ppm resonance and the 14.2 ppm resonance are equal in the benzonitrile-spiked C_6D_6 solution of **5**. When the spectrum of **5** is obtained in CD_2Cl_2-spiked benzonitrile, a single resonance at 14.0 ppm is observed. We postulate that the bound benzonitrile of **5** is labile and that the ^1H NMR spectrum obtained in C_6D_6 reflects an equilibrium between $Cp^*_2UI_2$ and **5**. We tentatively assign the downfield resonance at 18.0 ppm to the 30 Cp* hydrogens of $Cp^*_2UI_2$, in reasonable agreement with the 16.8 ppm resonance reported for the in-situ preparation of $Cp^*_2UI_2$.[38] Because of the overwhelming presence of the coordinating benzonitrile solvent, the ^1H NMR spectrum of **5** in CD_2Cl_2-spiked benzonitrile shows the Cp* resonance for **5** exclusively. The EI mass spectrum of crystals of complex **5** dissolved in toluene shows a molecular ion peak at $m/z = 762$ for $Cp^*_2UI_2$ and a peak at $m/z = 103$ for free benzonitrile, supporting the theory that benzonitrile binds weakly to $Cp^*_2UI_2$.

B. Addition of KTp* to $UI_4(N{\equiv}CPh)_4$ Solutions. Polypyrazolyl borate derivatives of uranium have been studied[29,41,44−59] for the last three decades, and like uranium cyclopetadienide compounds, these complexes are generally prepared from UCl_4. Two notable exceptions are the reactions of UI_4 with Tp (Tp = hydridotris(pyrazolyl)borate)[47] and Tp* (Tp* = hyridotris(3,5-dimethylpyrazolyl)borate).[29] In both cases, dissolution of UI_4 in THF followed by addition of the pyrazolylborate ligand results in the isolation of 4-iodobutoxide U(IV) species $Tp_2UI(O(CH_2)_4I)$ and $Tp^*UI_2(O(CH_2)_4I)$, respectively, because of ring opening of THF by UI_4. The increased solubility of **3** in organic solvents relative to the insolubility of both UI_4 and $UI_4(N{\equiv}CMe)_4$ prompted reactivity studies of **3** with KTp* in methylene chloride and toluene solutions.

Treatment of a red methylene chloride solution of **3** with 1.2 equiv of KTp* produces a yellow-green solution within 1 h of stirring at room temperature. Filtration to remove KI and excess KTp* followed by evaporation of the filtrate solution and washing with toluene, benzene, or ether to

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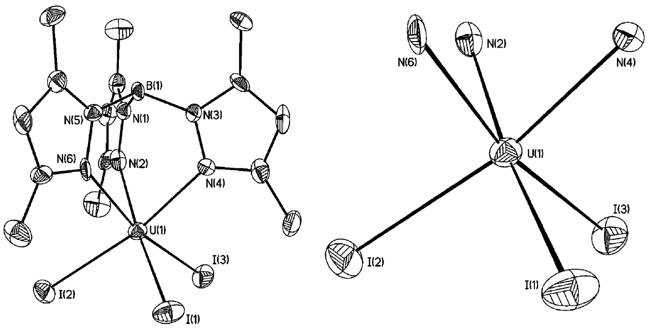

Figure 7. Thermal ellipsoid plot of Tp^*UI_3 (**6**) (left) and coordination geometry of U(IV) center (right) at the 35% probability level. Three cocrystallized toluene molecules are omitted. Selected bond lengths (Å): U(1)−N(2) = 2.446(9); U(1)−N(4) = 2.422(9); U(1)−N(6) = 2.425(9); U(1)−I(1) = 2.960(1); U(1)−I(2) = 2.973(1); U(1)−I(3) = 2.969(1). Selected bond angles (deg): I(1)−U(1)−I(2) = 93.54(4); I(2)−U(1)−I(3) = 94.96(5); I(3)−U(1)−I(1) = 95.91(4); N(2)−U(1)−N(6) = 77.2(3); N(6)−U(1)−N(4) = 78.2(3); N(4)−U(1)−N(2) = 78.8(3).

remove benzonitrile from the crude reaction mixture results in the isolation of Tp^*UI_3 (**6**) in 61% isolated yield as a brilliant green powder.

Dissolution of **6** in toluene and cooling to −38 °C produces crystals of Tp^*UI_3·3(toluene), and the crystal structure of Tp^*UI_3 is shown in Figure 7. The coordination environment of the uranium (IV) atom is approximately octahedral, with the three nitrogen donor atoms from the Tp* ligand forming one trigonal face of the octahedron and the three iodides forming another. The compound is almost isostructural to that of the previously reported Tp^*UCl_3, except for the expected longer U−X distances for U−I's which range between 2.957(1) and 2.971(1) Å, relative to the U−Cl's which range between 2.548(3) and 2.68(3) Å.[51] The ^1H NMR of complex **6** in CD_2Cl_2 is consistent with a C_{3v} symmetric paramagnetic complex in solution. The resonances at δ = 7.80, 5.49, and −7.71 ppm exist in a 1:3:3 ratio and agree with the resonances reported for spectroscopically characterized **6** formed by oxidation of Tp^*UI_2(THF) with iodine in toluene.[29] In addition, the ^{13}C NMR spectrum shows five resonances for the five inequivalent carbon environments in the bound Tp* ligand. The ^{11}B NMR spectrum shows a well-resolved doublet at δ = 22.0 ppm ($^1J_{B-H}$ = 141 Hz) for the Tp* B−H moiety. The UV−vis−NIR spectrum of Tp^*UI_3 in CH_2Cl_2 is shown in Figure 4.

Treatment of either crude or pure **6** with acetonitrile results in a rapid quantitative conversion to a mustard-yellow material. Crystals of $Tp^*UI_3(N{\equiv}CMe)$ (**7**) were obtained by vapor diffusion of hexanes into a CH_2Cl_2 solution of this mustard-yellow material, and the crystal structure is shown in Figure 8. Attempts to prepare *t*-Bu−N≡C and pyridine adducts of Tp^*UI_3 in a similar fashion were unsuccessful. When we attempted to prepare the pyridine adduct of **6** by dissolution in pyridine followed by vapor diffusion of hexanes, we isolated crystals which were analyzed as a $[Tp^*B]_2[UI_6]$ (**8**) decomposition product by X-ray diffraction. Similar degradation of the Tp* ligand to form 3,5-dimethylpyrazole-bridged dibora cations has been observed during the synthesis of electrophilic early transition-metal complexes.[52,60] The thermal ellipsoid plot of decomposition product **8** is included in the Supporting Information.

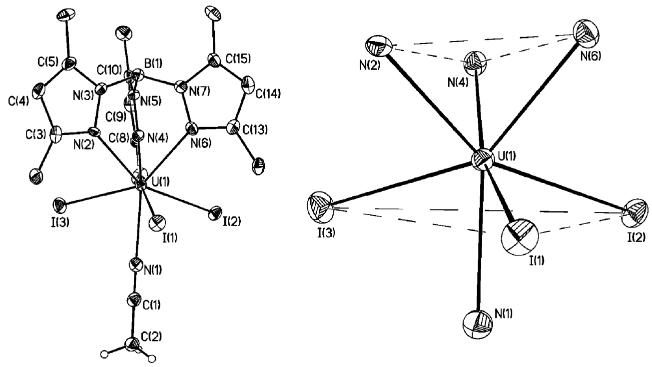

Figure 8. Thermal ellipsoid plot of $Tp^*UI_3(N{\equiv}CMe)$ (**7**) at the 35% probability level. Selected bond lengths (Å): U(1)−N(2) = 2.463(5); U(1)−N(4) = 2.455(5); U(1)−N(6) = 2.513(5); U(1)−I(1) = 2.9980(8); U(1)−I(2) = 3.0238(9); U(1)−I(3) = 3.3036(7); U(1)−N(1) = 2.557(6); N(1)−C(1) = 1.143(8). Selected bond angles (deg): I(1)−U(1)−I(2) = 101.89(1); I(2)−U(1)−I(3) = 117.44(2); I(3)−U(1)−I(1) = 115.42(2); I(1)−U(1)−N(1) = 73.3(1); I(2)−U(1)−N(1) = 73.2(1); I(3)−U(1)−N(1) = 72.2(1); N(2)−U(1)−N(6) = 77.2(3); N(6)−U(1)−N(4) = 78.2(3); N(4)−U(1)−N(2) = 78.8(3). The dashed lines are a visual aid representing two faces of the monocapped octahedron.

Analogous to the two Tp^*UCl_3(L) (L = THF,[52] O=P(O−$C_2H_3)_3$[53]) complexes which have been structurally characterized, the crystal structure of **7** contains a central uranium atom with monocapped octahedral geometry. The three N-donor atoms of Tp* and the three iodide atoms coordinate facially to the central uranium atom, and the acetonitrile N atom caps the face formed by the iodides. Despite the small size and the linear profile of the acetonitrile, the U(1)−N(1) distance of 2.557(6) Å is longer than either U−O distance of 2.546(4) or 2.373(7) Å from Tp^*UCl_3(THF) and Tp^*UCl_3(O=P(O−$C_2H_3)_3$), respectively, likely because of the oxophilicity of uranium. The average U−I distance in Tp^*UI_3 of 2.967(1) Å increases by 0.14−3.109(8) Å upon coordination of acetonitrile; however, it should be noted that the U(1)−I(3) distance is much longer, by ~0.3 Å, than the two 3.0 Å U−I distances in **7**. The average U−I distance increase from **6** to **7** is double that of the average 0.05 Å U−Cl distance increase observed upon coordination of the O-atom donors THF and O=P(O−$C_2H_3)_3$ to Tp^*UCl_3. The 0.05 Å lengthening of the average Tp* U−N distance appears to increase uniformly upon coordination of the Lewis bases to either $Tp^*U(X)_3$ compound.

The Tp* hydrogen signals of **7** in CD_2Cl_2 resonate at the same frequencies in the ^1H NMR spectrum as those for Tp^*UI_3, with the only difference in these spectra being a three-hydrogen singlet assigned to the methyl resonance of acetonitrile in **7**, which appears at 1.94 ppm. The ^{13}C NMR spectrum of **7** also differs by the appearance of a quartet carbon resonance assigned to the methyl carbon of the acetonitrile centered at 1.71 ppm. No resonance for the nitrile carbon was observed. Optical absorbance spectra of complexes **6** and **7** in CH_2Cl_2 solutions are superimposable. The ^{11}B NMR spectrum of **7** has a single resonance which appears as a doublet centered at δ = 22.2 ppm with ^1J_H = 89.5 Hz. We postulate that the 51 Hz difference between the $^1J_{B-H}$

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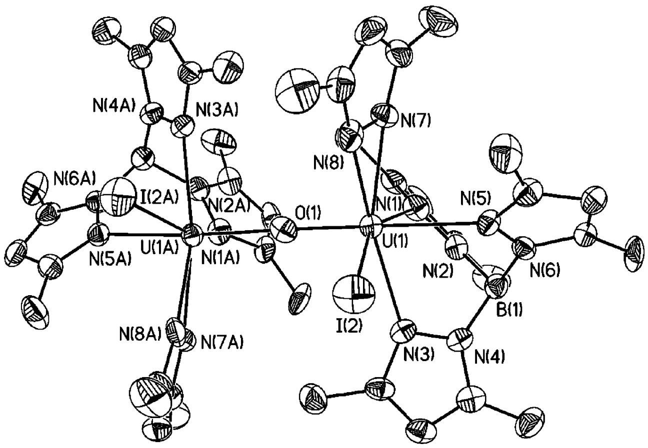

Figure 9. Thermal ellipsoid plot of [Tp*UI(dmpz)]$_2$[μ-O] at the 35% probability level. Selected bond length (Å): U(1)−O(1) = 2.098(1). Selected bond angle (deg): U(1)−O(1)−U(1A) = 166.7(5).

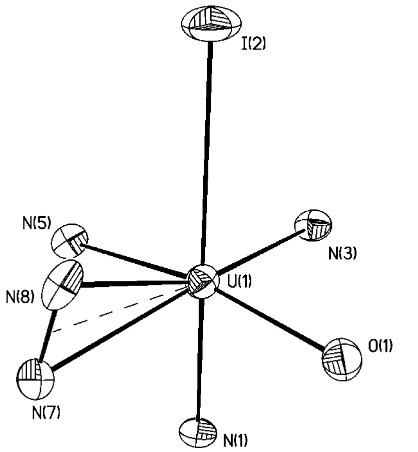

Figure 10. Thermal ellipsoid plot of the U(IV) coordination environment in [Tp*UI(dmpz)]$_2$[μ-O] (**9**). Selected bond lengths (Å): U(1)−O(1) = 2.098(1); U(1)−I(2) = 3.0650(9); U(1)−N(1) = 2.509(8); U(1)−N(3) = 2.543(8); U(1)−N(5) = 2.526(9); U(1)−N(7) = 2.390(8); U(1)−N(8) = 2.331(8); N(7)−N(8) = 1.38(1); [N(7)−N(7)$_{center}$]−U(1) = 2.257. Selected bond angles (deg): N(8)−U(1)−N(7) = 34.0(3); [N(8)−N(7)$_{center}$]−U(1)−N(1) = 99.9(3); [N(8)−N(7)$_{center}$]−U(1)−N(3) = 166.1(3); [N(8)−N(7)$_{center}$]−U(1)−N(5) = 87.8(3); [N(8)−N(7)$_{center}$]−U(1)−O(1) = 98.1(3); [N(8)−N(7)$_{center}$]−U(1)−I(2) = 95.9(3); N(1)−U(1)−I(2) = 156.5(2); N(5)−U(1)−O(1) = 163.8(4). The dashed line represents the pseudoaxis of the distorted octahedron passing through U(1) and the centroid of atom positions N(7) and N(8).

coupling constants observed for Tp*UI$_3$ and Tp*UI$_3$(N≡CMe) implies that the acetonitrile is coordinated to Tp*UI$_3$ in CD_2Cl_2 solution. However, the acetonitrile ligand of complex **7** is labile and can be removed from the uranium coordination sphere by repeated rinsing with ether to form **6**.

We attempted the addition of 1.2 equiv of KTp* to a toluene slurry of **3** at room temperature in a drybox and isolated Tp*UI$_3$ in low yield. We also performed the reaction using 2.2 equiv of KTp* in a Schlenk tube and heated the reaction for 12 h at 95 °C. The initially red slurry became brown with heating, and after several filtrations in a drybox, a grayish yellow filtrate was collected and placed in a freezer at −38 °C for 1 month. Large green crystals formed and were determined by single-crystal X-ray crystallography to be the oxo-bridged dinuclear uranium species [Tp*UI(dmpz)]$_2$[μ-O] (**9**) (dmpzH = 3,5-dimethylpyrazole). The residual filtrate was evaporated in vacuo, and **9** was isolated in 92% yield. We believe that this product forms because of the presence of adventitious water. Hydrolysis of the Tp* ligand has been observed during the preparation of analogous lanthanide(III) compounds of the type Tp*LnCl$_2$(THF)[61] to form Tp*LnCl$_2$(dmpzH) (dmpzH = 3,5-dimethylpyrazole; Ln = Y,[62] Yb,[63] or Lu[61]). We postulate that Tp*UI$_3$ facilitates the hydrolysis of an excess Tp* ligand present in the reaction to form Tp*UI$_3$(dmpzH), the uranium analogue of Tp*LnCl$_2$(dmpzH). A Tp*UI$_3$(dmpzH) intermediate could then undergo a series of formal HI elimination and hydrolysis reactions to ultimately form the dinuclear compound **9**.[64]

The crystal structure of **9** (Figure 9) shows the meso (*R*,*S*) stereoisomer of the dinuclear U(IV) complex with oxygen bridging two chiral centers. The μ-O is located at an inversion center; thus, both U atoms are symmetry related, with each binding to three nitrogen atoms from tridentate Tp*, two nitrogen atoms from the bidentate 3,5-dimethypyrazolide ligand, an iodide, and the bridging oxygen atom. If the dmpz ligand is considered to occupy a single coordination site, then the coordination environment around each U(IV) atom in **9** can be described as a distorted octahedron with the center of the dmpz N−N bond located 2.26(1) Å away from the U(IV) atom (Figure 10).

Few simple oxo-bridged dinuclear uranium species have been reported.[65−68] The 2.098(1) Å U−O distance in **9** is most comparable to the shorter 2.075(1) Å U−O distance reported for [Tp*UCl$_2$]$_2$[μ-O].[65] The 0.023(1) Å increase in U−O bond length can be ascribed to the larger steric encumbrance imparted by the dmpz and both iodides relative to three chlorides. The U−O−U angle of 166.7(5)° is almost identical to the 167.1(5)° angle found in [Cp*$_2$UCl]$_2$[μ-O][68] which, coincidently, has a comparable U−O distance of 2.13 Å.

The ^{1}H NMR spectrum of complex **9** is paramagnetically broadened and complicated. For the meso isomer of **9**, each "half" of the molecule is identical and one would expect to observe 12 resonances: three for each unique pyrazole ring of two equivalent Tp* ligands and three for each of the two equivalent dmpz ligands. We could assign only seven

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(64) One helpful referee correctly pointed out that there are many equally plausible mechanistic pathways to forming the μ-O complex **9**. For example, initial formation of (κ^3-Tp*)UI$_3$(κ^2-Tp*) could undergo hydrolysis to give (κ^3-Tp*)UI$_2$(OH)(κ^2-Tp*). Subsequent B−N cleavage would then give (κ^3-Tp*)(UI$_2$)(dmpz). Once some Tp*$^-$ has undergone B−N cleavage, any number of possible pathways could generate the final μ-O complex.
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resonances of equal intensity at $\delta = 70.22, 20.12, -2.74, -8.09, -14.10, -18.06$, and -39.18 ppm to three hydrogens each of either a Tp* methyl group or a dmpz methyl group. The NMR sample could contain either or both of the (*R*,*R*)-**9** or (*S*,*S*)-**9** diastereomers of (*R*,*S*)-**9**. Either one of these asymmetric stereoisomers would provide up to 24 different additional resonances in the spectrum. The electronic absorption spectrum of **9** is shown in Figure 4 for comparison to the other U(IV) iodides we have prepared.

Conclusion

Characterization of products from the oxidation of uranium metal with 1.3 equiv of iodine in nitrile solvents has been presented. When this reaction is carried out in acetonitrile, the mixed-valent U(III)/U(IV) complex $[U(N{\equiv}CMe)_9][UI_6]$ is isolated. In contrast, the same reaction in benzonitrile provides $UI_4(N{\equiv}CPh)_4$ as the only product. This U(IV) tetraiodide complex was prepared in synthetically useful quantities and characterized by single-crystal X-ray crystallography, NMR, Raman, FT-IR, and UV−vis−NIR spectroscopies. Heating $UI_4(N{\equiv}CPh)_4$ in benzonitrile solution to reflux generates $[UI(N{\equiv}CPh)_8][UI_6]$, a U(III)/U(IV) salt analogous to the product obtained by iodine oxidation in acetonitrile, as a decomposition product. The facile high-yield synthesis of $UI_4(N{\equiv}CPh)_4$, compared with the high-temperature furnace methods used to prepare UI_4 and UBr_4 or the harsh reducing conditions used to prepare UCl_4, and its solubility in organic solvents make it a useful UX_4 precusor. Treatment of a toluene solution of $UI_4(N{\equiv}CPh)_4$ with excess Cp*MgCl·THF provided $Cp^*{}_2UI_2(N{\equiv}CPh)$, and treatment with KTp* in CH_2Cl_2 solution cleanly provided both Tp^*UI_3 and $Tp^*UI_3(N{\equiv}CMe)$ depending on workup conditions. Addition of 2.2 equiv of KTp* to a toluene solution of $UI_4(N{\equiv}CPh)_4$ followed by prolonged heating at 95 °C, filtration, and crystallization led to the isolation of $[Tp^*UI(dmpz)]_2[\mu\text{-}O]$, which presumably resulted from the presence of adventitious water.

Acknowledgment. We thank the Heavy Element Chemistry Research Program, Chemical Sciences Division of the Office of Basic Energy Sciences, U.S. Department of Energy, for funding. The University of California operates LANL for the U.S. DOE under contract W-7405-ENG-36. We also thank the following generous colleagues: Dr. C. Drew Tait (Raman spectrum of $UI_4(N{\equiv}CPh)_4$), Dr. Warren Oldham (CV of $UI_4(N{\equiv}CPh)_4$), Dr. Jeffery Golden (Cp*MgCl·THF), UNC−Chapel Hill Professor Joseph Templeton (KTp*), and Dr.'s Carol Burns and Jaqueline Kiplinger for liberal use of their equipment.

Supporting Information Available: Tables of crystallographic data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anistotropic thermal parameters for compounds **1** and **3**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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