ORGANOMETALLICS

Exploring the Insertion Chemistry of Tetrabenzyluranium Using Carbonyls and Organoazides

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Supporting Information

ABSTRACT: The insertion chemistry of $U(CH_2C_6H_5)_4$ (1) was explored with acetone, benzophenone, mesityl azide, and 1-azidoadamantane. Using 2 equiv of acetone affords the double-insertion product $U[OC(CH_3)_2(CH_2C_6H_5)]_2$ - $(CH_2C_6H_5)_2(THF)_2$ (2), while using 4 equiv results in the tri-inserted enolate product U[OC(CH₃)₂(CH₂C₆H₅)]₃[OC- $(CH_3)CH_2$ (THF)₃ (3). Deuterium labeling experiments aided in the assignment of 2 and 3. With 4 equiv of benzophenone, insertion at all U-C bonds is noted, forming $U[OC(C_6H_5)_2(CH_2C_6H_5)]_4$ (4) and the THF adduct U[OC- $(C_6H_5)_2(CH_2C_6H_5)]_4(THF)$ (4-THF). Addition of 4 equiv of N₃Mes to 1 forms the tetrakis(triazenido)uranium(IV) complex U[CH₂(C₆H₅)NNN(Mes)- $\kappa^2 N^{1,2}$][CH₂(C₆H₅)-NNN(Mes)- $\kappa^2 N^{1,3}$], (5), while the same reaction with 1azidoadamantane generates the uranium(VI) trans-bis(imido) complex U(NAd)₂[CH₂(C₆H₅)NNN(Ad)- $\kappa^2 N^{1,3}$]₂(THF) (6). All species were characterized by ¹H NMR and infrared spectroscopy, with select examples being structurally characterized using single-crystal X-ray diffraction.



As the study of organoactinide complexes for smallmolecule activation has risen in recent years, so has the use of actinides, specifically uranium, for insertion chemistry. Because M-C insertion is an essential role in many catalytic transformations,¹⁻⁸ understanding this process for uranium is an important step toward the development of uranium-based catalysts.

While trivalent uranium compounds readily undergo radical reactions, uranium(IV) alkyls are a versatile and robust class of molecules for insertion chemistry. The uranium(IV) dimethyl species Cp*₂UMe₂ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienide) readily inserts carbon dioxide,⁹ acetone,¹⁰ carbodiimides,¹¹ nitriles,¹² diazoalkanes,¹³ and 1-azidoadamantane,¹¹ while the related tethered species [(η^5 -C₅Me₄SiMe₂CH₂- κ C)₂U] reacts similarly with carbon monoxide,¹⁴ carbodiimides,¹⁵ carbon disulfide,¹⁶ and 1-azidoadamantane.¹⁶

Our laboratory recently reported the synthesis of tetrabenzyluranium, $U(CH_2Ph)_4$ (1), a homoleptic uranium(IV) alkyl compound that engages in concerted carbon–carbon reductive elimination of bibenzyl in the presence of the redox-active α diimine ^{Mes}DAB^{Me} (^{Mes}DAB^{Me} = MesN=C(Me)C(Me)= NMes; Mes = 2,4,6-trimethylphenyl), highlighting its ability to perform fundamental organometallic reactions.¹⁷ Given the reactivity of these U–C bonds, this molecule presents a unique opportunity to study multiple migratory insertions on a single tetravalent uranium center. Herein, we present the reactivity of 1 toward acetone, benzophenone, mesityl azide, and 1azidoadamantane and the characterization of these products by ¹H NMR and infrared spectroscopies as well as by X-ray crystallography. The results presented here mark the first exploration of the reactivity of a uranium tetrakis(alkyl) toward insertion chemistry.

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 coldwell 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.¹⁸ Benzene- d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Benzophenone was recrystallized from diethyl ether and dried on the Schlenk line prior to use. Acetone- d_6 and 1-azidoadamantane were purchased from Sigma Aldrich and used without further purification. Acetone was purchased from Sigma Aldrich, dried over CaCl₂ and distilled. U(CH₂C₆H₅)₄ (1),¹⁷ 1- d_{28} ,¹⁷ and mesityl azide¹⁹ were prepared according to literature procedures.

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are

Received: March 11, 2013 **Published:** May 28, 2013 reported relative to the peak for SiMe₄ using ¹H (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 ¹H 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.

Single crystals 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 K α radiation ($\lambda = 1.54184$ Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.²⁰ The structures were solved using the structure solution program PATTY in DIRDIF99.²¹ Refinement was performed on a LINUX PC using SHELX-97.²⁰ The data were collected at a temperature of 150(1) K.

The capillary gas chromatography/mass spectrometry analyses were carried out using an Agilent 5975C (Agilent Laboratories, Santa Clara, CA) mass spectrometer system. The typical electron energy was 70 eV, with the ion source temperature maintained at 250 °C. The individual components were separated using a 30 m HP-5 capillary column (250 m i.d. \times 0.25 m film thickness). The initial column temperature was set at 35 °C (for 3 min) and programmed to reach 280 °C with a ramp of 10.0 °C/min. The flow rate was set at 1 mL/min and the injector set at 250 °C.

Synthesis of U[OC(CH₃)₂(CH₂C₆H₅)]₂(CH₂C₆H₅)₂(THF)₂ (2). A 20 mL scintillation vial was charged with 0.042 g (0.070 mmol) of 1 and approximately 5 mL of THF. While the mixture was stirred, 8.0 μ L (0.140 mmol) of acetone was added, resulting in a color change from dark red to brown within 5 min. Upon stirring for 30 min, the solvent was removed in vacuo, to yield a brown oil assigned as U[OC-(CH₃)₂(CH₂C₆H₅)]₂(CH₂C₆H₅)₂(THF)₂ (2). Yield: 0.065 g (0.067 mmol, 97%). The oily nature of 2 precluded reproducible elemental analysis. ¹H NMR (C₆D₆, 25 °C): δ –213.97 (504, 4H, CH₂), –21.88 (126, 4H), –17.79 (61, 2H, *p*-Ar-H), –17.35 (577, 8H, CH₂-THF), –16.86 (28, 2H, *p*-Ar-H), –12.53 (44, 4H), –7.68 (517, 8H, CH₂-THF), 8.46 (51, 4H), 25.99 (73, 4H), 83.85 (172, 12H, CH₃), 91.09 (161, 4H).

Synthesis of 2- d_{28} . With use of a procedure similar to that for 2, the product 2- d_{28} was prepared from 1- d_{28} and 2 equiv of acetone.

Synthesis of 2- d_{12} . With use of a procedure similar to that for 2, the product 2- d_{12} was prepared from 1 and 2 equiv of acetone- d_6 .

Synthesis of $U[OC(CH_3)_2(CH_2C_6H_5)]_3[OC(CH_3)CH_2](THF)_3$ (3). A 20 mL scintillation vial was charged with 0.064 g (0.106 mmol) of 1 and approximately 5 mL of THF. While the mixture was stirred, 31.2 μ L (0.425 mmol) of acetone was added, resulting in a color change from dark red to green-brown within 5 min. Upon stirring for 30 min, the solvent was removed in vacuo to yield a green-brown oil assigned as $U[OC(CH_3)_2(CH_2C_6H_5)]_3[OC(CH_3)CH_2](THF)_3$ (3). Yield: 0.090 g (0.099 mmol, 85%). The oily nature of 3 precluded reproducible elemental analysis. ¹H NMR (C₆D₆, 25 °C): δ -101.27 (43, 1H, p-Ar-H), -83.19 (24, 2H, CH₂-enolate), -73.93 (29, 2H, CH₂), -61.07 (19, 6H, CH₃), -9.26 (d, 7.2 Hz, 2H, o-Ar-H), 0.67 (t, 2H, m-Ar-H), 2.67 (31, 3H, CH₃-enolate), 6.60 (562, 24H, CH₂-THF) 7.82 (22, 6H, CH₃), 9.18 (t, 8 Hz, 1H, p-Ar-H), 9.99 (t, 7 Hz, 2H, m-Ar-H), 11.63 (t, 7 Hz, 1H, p-Ar-H), 12.83 (t, 7 Hz, 2H, m-Ar-H), 14.89 (d, 7 Hz, 2H, o-Ar-H), 22.15 (d, 7 Hz, 2H, o-Ar-H), 34.60 (17, 2H, CH₂), 47.61 (14, 6H, CH₃), 55.08 (19, 2H, CH₂).

Synthesis of 3- d_{21} **.** With use of a procedure similar to that for 3, the product 3- d_{21} was prepared from 1- d_{28} and 4 equiv of acetone.

Synthesis of 3- d_{23} . With use of a procedure similar to that for 3, the product $3 \cdot d_{23}$ was prepared from 1 and 4 equiv of acetone- d_6 .

Synthesis of $U[OC(C_6H_5)_2(CH_2C_6H_5)]_4(THF)$ (4-THF) and U-[OC(C₆H₅)₂(CH₂C₆H₅)]₄ (4). A 20 mL scintillation vial was charged with 0.062 g (0.103 mmol) of 1 and approximately 5 mL of THF. While the mixture was stirred, 0.070 g (0.412 mmol) of benzophenone was added, resulting in a color change from dark red to green within 5 min. After 1 h of stirring, the solvent was removed in vacuo to yield a green oil assigned as $U[OC(C_6H_5)_2(CH_2C_6H_5)]_4(THF)$ (4-THF). Trituration with diethyl ether and subsequently pentane (approximately 5 mL three times each) resulted in a gray-purple solid assigned as $U[OC(C_6H_5)_2(CH_2C_6H_5)]_4$ (4). Yield: 0.120 g (0.093 mmol, 91%). X-ray-quality crystals of 4-THF were obtained from cooling a concentrated solution in THF and pentane (10:1) to -35 °C. Due to the product being a mixture of 4 and 4-THF, reproducible elemental analysis was not obtained. ¹H NMR (C_6D_6 , 25 °C): δ –5.59 (98, 8H), 0.58 (32, 8H), 2.52 (26, 4H, *p*-Ar-*H*), 7.30 (21, 8H), 7.67 (21, 16H), 10.58 (88, 8H), 11.68 (31, 16H).

Synthesis of U[CH₂(C₆H₅)NNN(Mes)- $\kappa^2 N^{1,2}$][CH₂(C₆H₅)NNN- $(Mes)-\kappa^2 N^{1,3}]_3$ (5). A 20 mL scintillation vial was charged with 0.093 g (0.154 mmol) of 1 and approximately 5 mL of THF and cooled to -35 °C. While the mixture was stirred, 0.100 g (0.617 mmol) of mesityl azide was added. Upon stirring for 1 h, a color change from dark red to bright red occurred. The THF was removed in vacuo, and the residue was taken up in diethyl ether, filtered, and dried. A red solid was obtained. Recrystallization from a concentrated solution of diethyl ether at -35 °C gave orange-red crystals assigned as U[CH₂(C₆H₅)NNN(Mes)- $\kappa^2 N^{1,2}$][CH₂(C₆H₅)NNN(Mes)- $\kappa^2 N^{1,3}$]₃ (5). Yield: 0.124 g (0.099 mmol, 65%). X-ray-quality single crystals were obtained in the same manner. Compound 5 began to decompose after 12 h at room temperature in the solid state and thus would not survive shipping for elemental analysis. ¹H NMR (C_6D_6 , 25 °C): δ -27.26 (312, 18H, o-CH₃), -1.36 (5, 3H, p-CH₃), -1.31 (5, 1H, p-Ar-H), -0.94 (7, 6H), -0.14 (7, 9H, p-CH₃), 0.17 (32, 6H), 6.36 (t, 8 Hz, 3H, p-Ar-H), 6.49 (t, 7 Hz, 6H), 11.21 (26, 6H), 12.64 (21, 2H), 14.78 (21, 2H), 36.81 (71, 2H), 45.60 (645, 6H), 101.30 (429, 2H).

Synthesis of U(NAd)₂[CH₂(C₆H₅)NNN(Ad)- $\kappa^2 N^{1,3}$]₂(THF) (6). A 20 mL scintillation vial was charged with 0.052 g (0.086 mmol) of 1and approximately 5 mL of THF. While the mixture was stirred, 0.061 g (0.345 mmol) of 1-azidoadamantane was added and instantaneous N2 evolution occurred, as indicated by effervescence. Upon stirring for 1 h, a color change from dark red to orange-red occurred. The THF was removed in vacuo, and the residue was taken up in pentane, filtered, and dried. An orange-red solid was obtained. Recrystallization in a concentrated solution of diethyl ether at -35 °C gave orange crystals assigned as U(N-Ad)₂[CH₂(C₆H₅)NNN(Ad)- $\kappa^2 N^{1,3}$]₂(THF) (6). X-ray-quality single crystals were obtained in the same manner. Yield: 0.063 g (0.065 mmol, 70%). Compound 6 began to decompose after 12 h at room temperature in the solid state and thus would not survive shipping for elemental analysis. ¹H NMR (C_6D_6 , 25 °C): δ 0.60 (9, 12H), 0.99 (12, 12H), 1.63 (44, 6H), 1.88 (44, 12H), 2.35 (19, 6H), 2.72 (8, 12H), 3.45 (1072, 4H, CH₂-THF), 4.87 (111, 4H, CH₂-THF), 6.20 (7, 4H, CH₂(C₆H₅)), 7.10 (t, 9 Hz, 2H, p-Ar-H), 7.34 (t, 8 Hz, 4H, m-Ar-H), 7.96 (d, 6 Hz, 4H, o-Ar-H).

Crossover Experiment of 1 and 1- d_{28} with 1-Azidoadamantane. A 20 mL scintillation vial was charged with 0.030 g (0.050 mmol) of 1, 0.031 g (0.050 mmol) of 1- d_{28} , and 5 mL of THF. While the mixture was stirred, 0.071 g (0.400 mmol) of 1-azidoadamantane was added and instantaneous N₂ evolution occurred, as indicated by effervescence. Upon stirring for 1 h, a color change from dark red to orange-red occurred, indicating formation of 6. The resulting solution was filtered through an alumina column using THF to separate the uranium-containing material from the organic products (pale orange). Capillary gas chromatography/mass spectrometry analyses showed the formation of a statistical mixture of bibenzyl (m/z 182), bibenzyl- d_7 (m/z 189), and bibenzyl- d_{14} (m/z 196).

RESULTS AND DISCUSSION

The reactivity for $U(CH_2Ph)_4$ (1) toward migratory insertion was first tested with carbonylated substrates, as the oxophilicity of uranium was presumed to be an important driving force. Compound 1 was treated with 2 equiv of acetone, which afforded a dark brown oil after workup. The infrared spectrum of the product did not show a carbonyl absorption. The ¹H



NMR spectrum contained 11 resonances ranging from -213.97 to 91.09 ppm, supporting a C_2 -symmetric molecule in solution that is consistent with two acetone insertions. A key resonance appears at -213.97 ppm (4H) for the U–CH₂ linkages of the two unreacted benzyl groups, similar to the case for Cp*Cp₂U(CH₂C₆H₅), which has a U–CH₂ resonance assigned at -229.58 ppm.²² The other diagnostic singlet appears at 83.85 ppm (12H) for equivalent CH₃ groups of two inserted acetone molecules, leading to the assignment of the brown product as U[OC(CH₃)₂(CH₂C₆H₅)]₂(CH₂C₆H₅)₂(THF)₂ (2) (Scheme 1).

Further support for the assignment of the acetone resonance of **2** was gained by deuteration in the preparation of $U[OC(CH_3)_2(CD_2C_6D_5)]_2(CD_2C_6D_5)_2](THF)_2$ (**2**-**d**₂₈) and $U[OC(CD_3)_2(CH_2C_6H_5)]_2(CH_2C_6H_5)_2](THF)_2$ (**2**-**d**₁₂). **2d**₂₈ was synthesized using **1**-**d**₂₈ and acetone and shows only the resonances for inserted acetone methyl groups and coordinated THF in the ¹H NMR spectrum. Using 2 equiv of acetone-*d*₆ with **1** forms the isotopologue, **2**-*d*₁₂, causing the resonance for the acetone methyls at 83.85 ppm to disappear from the ¹H NMR spectrum in comparison to the spectra for **2** and **2**-*d*₂₈. All other expected resonances for **2** are present in the ¹H spectrum of **2**-*d*₁₂. Compound **1** reacts similarly to Tp₂UCl-(CH₂SiMe₃) and Tp₂U(CH₃)₂, which insert 1 and 2 equiv of acetone to form Tp₂UCl(OC(CH₃)₂CH₂SiMe₃) and Tp₂U-(OCMe₃)₂, respectively.²³

Interestingly, the addition of only 1 equiv of acetone to 1 does not result in a single insertion but produces 2 in $\sim 50\%$ yield. Because all four benzyl ligands are not activated in the preparation of 2, two alkyls remain for further reactivity. Thus, 1 was treated with 4 equiv of acetone under the same reaction conditions, which produced a green-brown oil, 3. The ¹H NMR spectrum of 3 is paramagnetically shifted and broadened with 18 resonances ranging from -101.27 to 55.08 ppm but does not display the symmetry for the expected tetrainsertion product. Rather, it appears that a non-insertion pathway is operative in the synthesis of 3. To test this, 3 was prepared in a sealed NMR tube; analysis revealed the formation of 1 equiv of toluene upon acetone addition, supporting protonation of a benzyl group by the acidic methyl protons. This has been previously observed for f-block elements,²⁴⁻²⁶ where subsequent rearrangement forms an enolate ligand. On the basis of this, compound 3 is assigned as U[OC- $(CH_3)_2(CH_2C_6H_5)]_3[OC(CH_3)CH_2](THF)_3$ (3), which contains three alkoxide ligands formed from acetone insertions as well as an enolate ligand.

The two isotopologues $U[OC(CH_3)_2(CD_2C_6D_5)]_3[OC (CH_3)CH_2](THF)_3$ (3-d₂₁) and $U[OC(CD_3)_2(CH_2C_6H_5)]_3$ - $[OC(CD_3)CD_2](THF)_3$ (3-d₂₃) were synthesized using 1-d₂₈ and acetone- d_{6} , respectively, to elucidate the NMR data. ¹H NMR spectroscopic analysis of $3-d_{21}$ showed five resonances at -61.07, 7.82, 47.61, 2.67, and -83.19 ppm (6:6:6:3:2). The first three resonances represent three equivalent CH_3 pairs for the three inserted acetone molecules, while the last two are assigned as a single CH_3 and a CH_2 , respectively, for the enolate ligand. As expected, these five resonances derived from the acetone molecules do not appear in the ¹H NMR spectrum of 3- d_{23} . In addition to these resonances, 13 signals are found for 3, characteristic of the three inequivalent benzyl groups and the three coordinated THF molecules. Detailed assignments are presented in the Experimental Section. The THF ligands in 3 are labile in solution, and their resonances weaken with addition of THF- d_8 to an NMR tube sample, indicating solvent exchange on the NMR time scale.

The preference for enolate formation over acetone insertion is attributed to the increased steric bulk at uranium following acetone insertions. This is supported by the report of the isolated uranium(III) enolate species $Tp*_2U(OC(CH_2)-CH_3)$,²⁴ which forms from protonation of the sterically protected benzyl group in $Tp*_2UCH_2Ph$. An enolate intermediate has also been proposed in the formation of the lanthanum aldolate $Cp*_2Ln(OCMe_2CH_2C(O)Me)$.²⁵ For 3, enolate formation is preferred, as adding 3 equiv of acetone to 1 produces only 3 in reduced yield, with no evidence for the triinserted product. Furthermore, there is no evidence for aldolate formation in the synthesis of 3.

Benzophenone was also used to probe the insertion chemistry of 1, as it was hypothesized that the lack of acidic protons would favor insertion. Upon addition of 4 equiv of benzophenone to a red THF solution of 1, a color change to green was observed; however, workup resulted in isolation of a gray-purple solid. IR spectroscopy of the solid showed no absorptions characteristic of a carbonyl moiety, supporting benzophenone insertion.

This assertion was supported by ¹H NMR spectroscopy, which showed a paramagnetically shifted and broadened spectrum with seven resonances ranging from -5.59 to 11.68 ppm. Two resonances at 7.67 and 11.68 ppm (16H)







Figure 1. Molecular structures of 4-THF (a), 5 (b), and 6 (c) shown with 30% probability ellipsoids. Solvent molecules and hydrogen atoms have been omitted for clarity.

correspond to meta and ortho Ar-H protons of benzophenone, while the signal at 2.52 ppm (4H) is consistent with *p*-Ar-H protons of the benzyl substituent. The remaining four resonances integrate to eight protons each and are not assignable on the basis of integration. The number of resonances and symmetry support that the product is the result of benzophenone insertion at each U–C bond, $U[OC(C_6H_5)_2(CH_2C_6H_5)]_4$ (4) (Scheme 1).

Initial attempts to generate a single crystal of 4 suitable for Xray diffraction from hydrocarbon solvents were unsuccessful. However, upon addition of THF to 4, a color change from gray-purple to green ensued. Removing THF under reduced pressure regenerated the gray-purple compound, supporting that the green product is the THF adduct U[OC- $(C_6H_5)_2(CH_2C_6H_5)]_4(THF)$ (4-THF) (Scheme 1). Compound 4 is capable of cycling between colors at least five times with little decomposition observed.

Cooling a concentrated THF/pentane solution (10:1) of 4-THF resulted in pale green crystals. Single-crystal X-ray analysis showed a five-coordinate product, with a THF ligand and four alkoxides formed by insertion of benzophenone (Figure 1a; key structural parameters are given in Table 1). The uranium center

Table 1. Structural Parameters for 4-THF

| bond | length (Å) | connection | angle (deg) |
|--------|------------|------------|-------------|
| U1-01 | 2.219(6) | O51-U1-O4 | 174.8(2) |
| U1-O2 | 2.123(6) | O3-U1-O2 | 118.7(3) |
| U1-O3 | 2.118(6) | O3-U1-O1 | 111.8(2) |
| U1-04 | 2.127(5) | O3-U1-O4 | 99.6 (2) |
| U1-051 | 2.485(7) | O3-U1-O51 | 85.4(2) |
| | | | |

is pseudo trigonal bipyramidal, with U–O distances of 2.219(6), 2.123(6), 2.118(6), and 2.127(5) Å for the anionic alkoxide ligands. All are on the order for monoanionic U–O bonds. The last three are similar to U(OCMe₂CH₂{C-(NCH₂CH₂NR)})(N(SiMe₃)₂)₂ (R = 2,6-iPr₂C₆H₃) of 2.122(3) Å²⁷ and [((^{Ad}ArO)₃tacn)U^{IV}(OCPhPh–CPh₂O)-U^{IV}((^{Ad}ArO)₃tacn)] ((^{Ad}ArO)₃tacn = trianion of 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane) of 2.109(4) Å.²⁸ The U–OS1 bond distance of 2.485(7) Å is consistent with the distances in UCl₄(THF)₃.²⁹

The benzophenone insertion by 1 is similar to that observed for $((Me_3Si)_2N)_3UCH_3$ in the formation of $((Me_3Si)_2N)_3UOCPh_2CH_3^{30}$ and reminiscent of aldehyde insertion shown by Eisen and co-workers to be a key step in thorium-mediated catalytic aldehyde dimerization.³¹ Thus, tetravalent $U(CH_2Ph)_4$ facilitates four insertions at a single uranium center, with no evidence for radical chemistry. The insertion chemistry is driven by replacing four reactive U–C bonds with four strong U–O bonds. Using 1, 2, or 3 equiv of benzophenone did not result in the mono-, di-, or tri-inserted products; instead, compound 4 was formed in lower yields.

The synthesis of 4 by carbonyl insertion diverges from products formed with uranium(III) centers and benzophenone. In these systems, C–O reduction to form a benzophenone radical intermediate is noted, followed by coupling with a nearby radical species. The result is an oxidized uranium center with a new U–O anionic bond.^{28,32} Therefore, the formation of 4 marks a rare example where structural insight is provided and highlights the important role the uranium oxidation state plays in the reactivity with carbonylated substrates.

Organoazides were also studied with 1 to determine if insertion is favored over oxidation. Addition of 4 equiv of mesityl azide to 1 at -35 °C results in a color change from dark red to orange-red. After workup and recrystallization, the product, 5, was obtained as an orange-red solid (Scheme 1). Although no nitrogen evolution was noted during the reaction, IR spectroscopy of 5 also did not show an azide absorption, supporting that insertion occurred to form 1-benzyl-3mesityltriazenido ligands. A symmetric tetrainserted product analogous to 4 would show a ¹H NMR spectrum with seven resonances. However, the spectrum showed 14 paramagnetically shifted and broadened signals ranging from -27.26 to 101.30 ppm.

To gain insight into the unexpected ¹H NMR spectrum, the molecular structure of **5** was determined by X-ray crystallog-raphy. Single crystals were grown from a concentrated solution of diethyl ether at -35 °C (Figure 1b; key structural parameters are given in Table 2). Analysis revealed the structure as the

Table 2. Structural Parameters for 5

| bond | length (Å) | bond | length (Å) |
|--------|------------|--------|------------|
| U1-N21 | 2.410(5) | U1-N12 | 2.516(5) |
| U1-N31 | 2.436(5) | U1-N13 | 2.297(5) |
| U1-N41 | 2.421(5) | U1-N42 | 2.939(5) |
| U1-N23 | 2.485(5) | U1-N22 | 2.953(5) |
| U1-N33 | 2.479(5) | U1-N32 | 2.959(6) |
| U1-N43 | 2.433(5) | | |
| | | | |

eight-coordinate, distorted bicapped trigonal prismatic tetraazenido uranium compound $[CH_2(C_6H_5)NNN(Mes)-\kappa^2N^{1,2}]$ - $U[CH_2(C_6H_5)NNN(Mes)-\kappa^2N^{1,3}]_3$ (5). One triazenido ligand is coordinated in a $\kappa^2N^{1,2}$ fashion, while the other three are coordinated in a $\kappa^2N^{1,3}$ fashion. With the two different ligand hapticities in 5 established, the complicated ¹H NMR spectrum was completely assigned (details in the Experimental Section).

The U–N distances for the three $\kappa^2 N^{1,3}$ ligands in 5, ranging from 2.410(5) to 2.485(5) Å, are consistent with full delocalization over the triazenido ligand. In analogy to 1, Evans recently reported 1-azidoadamantane insertion into the U-C σ bonds of Cp*₂U(Me)₂ to generate Cp*₂UMe[(Me)-NNN(Ad)- $\kappa^2 N^{1,3}$].¹¹ Although structural parameters could not be established for this compound, substitution of the methyl group yields $Cp_{2}^{*}UX[(Me)NNN-(Ad)-\kappa^{2}N^{1,3}]$ (X = I, Br, OTf), all of which have been crystallographically characterized.³³ This family has U–N distances ranging from 2.371(4) to 2.460(2) Å, which are on the order of those for 5. The $\kappa^2 N^{1,2}$ -triazenido ligand in 5 has significantly different U-N distances of 2.297(5) and 2.516(5) Å, suggesting one anionic and one dative U-N interaction as in the uranium(IV) hydrazonido compound $Cp*_2U[\eta^2(N,N')-RNN=CPh_2]_2$, which has U-N anionic bonds ranging from 2.275(17) to 2.317(8) Å and U-N dative interactions from 2.469(8) to 2.526(16) Å.¹³

Formation of **5** once again demonstrates a rare example of four insertions at a monomeric uranium alkyl species. However, compound **5** is not thermally stable, decomposing at room temperature in both the solution and solid states over a 12 h period, to generate bibenzyl and intractable uranium products. Exposure to light does not initiate or accelerate this process. Addition of 1, 2, or 3 equiv of mesityl azide to 1 generates **5** in lesser yields, similar to the benzophenone case. The insertion chemistry for N₃Mes is in contrast to that observed in the case of trivalent uranium, where addition of 1 equiv of N₃Mes to $Tp*_2UCH_2Ph$ and $Tp*U(CH_2Ph)_2$ results in oxidation to the respective uranium(IV) species $Tp*_2UNMes$ and $Tp*U-(CH_2Ph)(NMes)$, with extrusion of $1/_2$ equiv of bibenzyl.³⁴

Compound 1 was also treated with 4 equiv of 1azidoadamantane (AdN_3) to determine the generality of the azide insertion reaction. Upon addition to 1, immediate evolution of N_2 was noted, supporting the hypothesis that at least one imido moiety was formed (Scheme 1). Workup produced an orange-red solid, **6**, that is stable for 12 h in both the solution and solid states but eventually decomposed to a mixture of organic products, including adamantylamine. Again, IR spectroscopy showed no azide stretches.

Surprisingly, analysis by ¹H NMR spectroscopy revealed a diamagnetic spectrum with 12 resonances ranging from 0.60 to 7.96 ppm, indicative of oxidation to uranium(VI). A resonance assignable to bibenzyl (1 equiv vs ferrocene internal standard) is also visible. On the basis of the N₂ and bibenzyl extrusions, compound **6** is assigned as the uranium bis(imido) bis(triazenido) species, $U(NAd)_2[CH_2(C_6H_5)-NNN(Ad)-\kappa^2N^{1,3}]_2(THF)$. Thus, 2 equiv of azide serves to oxidize the uranium center, while the remaining two benzyls undergo U–C bond insertion. A key resonance at 6.20 ppm (4H) is assignable to the methylene CH_2 of the newly formed triazenido ligands. All other resonances are accounted for and assigned (Experimental Section).

Further characterization of **6** by X-ray crystallography was employed to establish the hapticity of the triazenido ligands. Cooling a concentrated solution of **6** in diethyl ether at -35 °C afforded suitable orange-red crystals (Figure 1c). Structural parameters (Table 3) support a seven-coordinate uranium

Table 3. Structural Parameters for 6

| bond | length (Å) | bond | length (Å) |
|------------------------|-----------------|------------------------------|-----------------|
| U1-N1 | 2.440(7) | U1-N7 | 1.903(10) |
| U1-N3 | 2.507(8) | U1-N8 | 1.912(9) |
| U1-N4 | 2.446(8) | U1-01 | 2.499(6) |
| U1-N6 | 2.482(8) | | |
| connection | avg angle (deg) | connection | avg angle (deg) |
| N7-U1-N8 | 173.4(3) | N_{eq} -U1- $N_{adjacent}$ | 61.8 |
| N_{ax} -U1- N_{eq} | 91.2 | $O1-U1-N_{adjacent}$ | 87.5 |

center in a distorted-pentagonal-bipyramidal geometry with two adamantyl imido ligands and two $\kappa^2 N^{1,3}$ -triazenido ligands. The two adamantyl imido ligands are *trans* with a near-linear N–U– N angle of 173.4(3)° and serve as the caps for the bipyramid, with the remaining five atoms forming the pentagonal plane. Compound **6** has U–N distances for the triazenido ligands of 2.440(7), 2.507(8), 2.446(8), and 2.482(8) Å, which compare well with those of **5** and Cp*₂UX[(Me)NNN(Ad)- $\kappa^2 N^{1,3}$].³³ The two *trans* imido ligands in **6** have U–N distances of 1.903(10) and 1.912(9) Å, on the order of that for the recently prepared U(VI) bis(imido) complex [Li(THF)]₂[U-(N^tBu)₂(NH^tBu)₄] (1.915(5) Å).³⁵

Compound **6** represents the first example of a uranium(VI) triazenido species and highlights the striking difference in insertion vs oxidation with the reactivity of N_3 Mes and N_3 Ad with **1**. Furthermore, the formation of **6** marks an additional synthetic route to access the *trans*-bis(imido) uranyl analogues studied by Boncella and co-workers.^{36–39}

A crossover experiment was performed to determine if a radical mechanism is operative in bibenzyl formation. An equimolar THF solution of 1 and $1-d_{28}$ was treated with 8 equiv of N₃Ad. Separation of the organics by filtration over an alumina column and analysis by GC-MS revealed the formation of bibenzyl, bibenzyl- d_7 , and bibenzyl- d_{14} . The observed crossover supports homolytic cleavage and radical coupling of benzyl groups from 1, which is in contrast to the concerted

reductive elimination which has been previously established for this molecule. $^{\rm 17}$

The chemistry of the uranium-carbon bonds of tetrabenzyluranium reported herein highlight the diverse reactivity of uranium(IV) alkyl species. With no ancillary ligands present, all four U-C bonds are reactive, readily undergoing insertion, protonation, or homolytic bond scission, depending on the substrate, to generate sterically saturated products. In all cases, the reactivity of the tested substrates with 1 diverges from that of trivalent uranium. The results presented here establish that ancillary ligands are not necessary for stabilizing the uranium center to facilitate insertion chemistry. These studies also show that uranium(IV) centers can support isolable yet reactive alkyl groups, facilitating four insertions at a single uranium center, which has not previously been observed. Thus, tetravalent organouranium species can perform fundamental reactions that are key steps for bond formation important to organometallic transformations.

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for **2-THF**, **5**, and **6**. 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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