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Functionalization of Carbon Dioxide and Carbon Disulfide Using a Stable Uranium(III) Alkyl Complex

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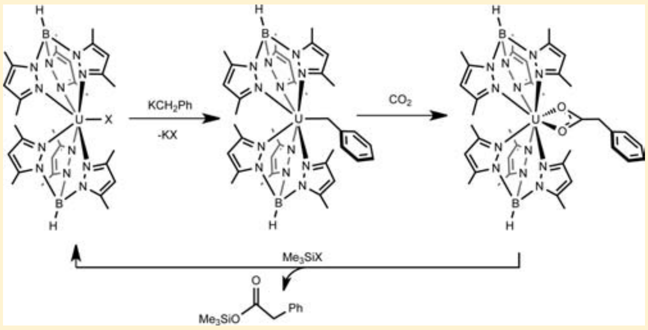
S *Supporting Information*

ABSTRACT: A rare uranium(III) alkyl complex, Tp*$_2$U(CH$_2$Ph) (**2**) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate), was synthesized by salt metathesis from Tp*$_2$UI (**1**) and KCH$_2$Ph and fully characterized using ^{1}H NMR, infrared, and electronic absorption spectroscopies as well as X-ray crystallography. This complex has a uranium−carbon distance of 2.57(2) Å, which is comparable to other uranium alkyls reported. Treating this compound with either carbon dioxide or carbon disulfide results in insertion into the uranium−carbon bond to generate Tp*$_2$U(κ^2-O$_2$CCH$_2$Ph) (**3**) and Tp*$_2$U(SC(S)CH$_2$Ph) (**4**), respectively. These species, characterized spectroscopically and by X-ray crystallography, feature new carboxylate and dithiocarboxylate ligands. Analysis by electronic absorption spectroscopy supports the trivalent oxidation state of the uranium center in both of these derivatives. Addition of trimethylsilylhalides (Me$_3$SiX; X = Cl, I) to **3** results in the release of the free silyl ester, Me$_3$SiOC(O)CH$_2$Ph, forming the initial uranium monohalide species, Tp*$_2$UX, which can then be used over multiple cycles for the functionalization of carbon dioxide.



INTRODUCTION

Carbon dioxide and carbon disulfide activation using transition-metal alkyls has been extensively studied, including stoichiometric and catalytic reactions that incorporate these molecules into various acids and esters.[1] Uranium(III) is an attractive platform for activation of these molecules given the ability of this metal to effectively reduce these and other small molecules with similarly strong bonds,[2] however, difficulties in accessing low-valent uranium alkyl species have precluded extensive studies of such species with CO$_2$ and CS$_2$. While the synthesis of a variety of uranium(IV) alkyls[3] has been successful, trivalent uranium alkyls are rare by comparison, as these species can be plagued by rapid disproportionation.[4] To date, only two examples[5a] of isolable uranium(III) alkyl compounds have been reported, U(CH(SiMe$_3$)$_2$)$_3$[5b] and Cp*$_2$U(CH(SiMe$_3$)$_2$) (Cp* = η^5-1,2,3,4,5-pentamethylcyclopentadienide).[6] These species both make use of the sterically bulky bis(trimethylsilyl)methyl substituent to impart stability.

Carbon dioxide insertion has been demonstrated for tetravalent U−N[7] and U−S[8] bonds, however, very few examples exist for insertion into uranium−carbon bonds. Recently, Evans has reported the formation of both Cp*$_2$U(κ^2-O$_2$CC≡CPh)$_2$[9a] and Cp*$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2-N,N']U(κ^2-O$_2$CMe),[9b] resulting from the insertion of CO$_2$ into tetravalent U−C bonds at high pressures (80 psi). Marks has shown the utility of uranium(IV) alkyls in carbon dioxide functionalization chemistry with insertion into both methyls of Cp*$_2$UMe$_2$ to form the bis(cyclopentadienyl) uranium(IV) bis(acetate) derivative.[10] In these cases using uranium, further functionalization of the carbon dioxide fragment has proven difficult, as the extreme oxophilicity of this metal prevents facile dissociation of the organic fragment from the uranium center.

Even less is known about the reactivity of carbon dioxide's sulfur analogue, carbon disulfide. Uranyl species react readily with CS$_2$ when paired with potassium hydroxide and an amine to make the corresponding dithiocarbamate ligands,[11] however, little is known about the reactivity with low-valent uranium species. One example with trivalent uranium, reported by Andersen, shows that (Cp^R)$_3$U(THF) (Cp^R = η^5-C$_5$H$_4$R; R = Me, SiMe$_3$) reduces CS$_2$ by one electron, producing the uranium(IV) bridging carbon disulfide species (Cp^R)$_3$U(μ-η^1,η^2-CS$_2$).[12] Insertion chemistry for CS$_2$ has only been observed for the U−N and U−S bonds of the respective tetravalent species, Cp$_2$U(NEt$_2$)$_2$[13] and Cp*$_2$U(S^{t}Bu)$_2$.[8] No CS$_2$ insertions into uranium−carbon bonds have been previously reported, thus uranium is not currently known to mediate C−C bond formation with CS$_2$.

To direct the highly reducing nature of uranium(III) toward the reduction and activation of the thermodynamically strong bonds in carbon dioxide (CO$_2$) and carbon disulfide (CS$_2$), we set out to synthesize and characterize a new example of a uranium(III) alkyl species supported by the bis(hydrotris(3,5-dimethylpyrazolyl)borate) ligand scaffold (Tp*). This bis(ligand) framework has been shown to effectively support a variety of low-valent uranium species[14] by preventing disproportionation, a common side reaction for uranium(III) alkyls.[4] Herein we report a new trivalent uranium alkyl complex, its reactivity with carbon dioxide and carbon disulfide,

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and the functionalization of the organic fragment, including its removal from the uranium center.

■ 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.[15] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze−pump−thaw cycles. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. Benzyl potassium was prepared according to literature procedures.[16] Anhydrous carbon disulfide (anhydrous, 99.9%), chlorotrimethylsilane and iodotrimethylsilane were purchased from Sigma Aldrich and dried over CaH_2 prior to use. Carbon dioxide (99.8%) was purchased from Sigma Aldrich and used as received. Depleted uranium was purchased from Manufacturing Sciences in Oak Ridge, TN. Tp^*_2UI (**1**) was prepared according to literature procedures.[17]

^1H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz (see Supporting Information for more information). All chemical shifts were reported relative to the peak for $SiMe_4$ 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, 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. Electronic absorption measurements were recorded at 294 K in THF in sealed 1 cm quartz cuvettes with a Jasco V-670 spectrophotometer.

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 Kα radiation ($\lambda = 1.54184$ A). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.[18] The structures were solved using the structure solution program PATTY in DIRDIFF99.[19] Refinement was performed on a LINUX PC using SHELX-97.[18] The data were collected at a temperature of 150(1) K.

Preparation of $Tp^*_2U(CH_2Ph)$ (2). A 20-mL scintillation vial was charged with 0.437 g (0.45 mmol) of **1** and approximately 10 mL of diethyl ether and cooled to −35 °C. In a separate vial, 0.065 g (0.50 mmol) of KCH_2Ph was dissolved in 5 mL of THF forming an orange solution. While stirring, the benzyl potassium solution was added dropwise to the purple uranium solution, causing an immediate color change to dark green. After stirring overnight, the volatiles were removed in vacuo. The residue was dissolved in toluene, filtered over Celite, and dried to produce a green solid (0.365 g, 0.42 mmol, 87%). Elemental analysis of $C_{37}H_{51}N_{12}B_2U$: Calculated, C, 48.12; H, 5.57; N, 18.20. Found, C, 47.87; H, 5.69; N, 18.09. ^1H NMR (C_6D_6, 25 °C): −11.10 (29, 18H, CH_3), −2.85 (7, 18H, CH_3), −0.28 (336, 2H, B-*H*) 7.12 (9, 6H, pyrazole-C*H*), 10.80 (17, 1H, phenyl-*para*-C*H*), 17.68 (17, 2H, phenyl-C*H*), 21.35 (171, 2H, CH_2), 26.21 (33, 2H, phenyl-C*H*).

Preparation of $Tp^*_2U(\kappa^2\text{-}O_2CCH_2Ph)$ (3). In a glovebox, a thick walled glass vessel was charged with **2** (0.100 g, 0.109 mmol) and 10 mL of THF. While frozen, the vessel was evacuated on a Schlenk line. After warming to room temperature, 1 atm of CO_2 was added to the vessel while stirring, resulting in an immediate color change from dark green to bright green. The solution was stirred under a CO_2 atmosphere for an additional 30 min. The volatiles were removed in vacuo, yielding a bright-green powder (0.103 g, 0.106 mmol, 97%). Elemental analysis of $C_{38}H_{51}N_{12}O_2B_2U$: Calculated, C, 47.17; H, 5.31; N, 17.37. Found, C, 46.97; H, 5.43; N, 17.20. ^1H NMR (C_6D_6, 25 °C): −8.76 (91, 18H, Tp*-CH_3), −0.96 (5, 18H, Tp*-CH_3), 0.90 (2H, B-*H*), 7.14 (30, 6H, Tp*), 8.73 (d, *J* = 7.2 Hz, 1H, C*H* *p*-phenyl), 9.50 (t, *J* = 8.1 Hz, 2H, C*H* *m*-phenyl), 15.67 (t, *J* = 7.8 Hz, 2H, C*H* *o*-phenyl), 17.11 (11, 2H, −CH_2). IR = 2556, 2526 cm^{-1} (B-H).

$Tp^*_2U(SC(S)CH_2Ph)$ (4). A 20 mL scintillation vial was charged with 0.100 g of **2** (0.108 mmol) and approximately 3 mL of THF. The solution was shaken vigorously and cooled to −35 °C. In a separate vial, 6.5 μL (0.008 mg, 0.108 mmol) of CS_2 was dissolved in approximately 3 mL of pentane and cooled to −35 °C. The pentane CS_2 solution was layered on top of the dark-green (**2**) solution and placed carefully back in the freezer without mixing of the layers. After 16 h, crystalline solid had precipitated. The solution was decanted, and the solid was washed with cold pentane. Residual solvents were removed in vacuo leaving a dark-green powder (0.067 g, 0.070 mmol, 62%). Due to the instability of **4**, reliable elemental analysis could not be obtained as the samples were not stable for shipping. ^1H NMR (C_6D_6, 25 °C): −20.78 (64, 6H, Tp*-CH_3), −12.05 (32, 6H, Tp*-CH_3), −1.13 (26, 6H, Tp*-CH_3), 0.56 (28, 6H, Tp*-CH_3), 2.27 (2H, CH_2Ph), 2.99 (53, 6H, Tp*-CH_3), 3.30 (46, 2H, Tp*-C*H*), 3.43 (43, 6H, Tp*-CH_3), 4.92 (205, 2H, B-*H*), 7.24 (6, 6H, Tp*-C*H*), 7.48 (t, *J* = 6.9 Hz, 2H, C*H* *m*-phenyl), 7.60 (t, *J* = 8.7 Hz, 1H, C*H* *p*-phenyl), 10.30 (d, *J* = 7.2 Hz, 2H, C*H* *o*-phenyl), 11.81 (46, 2H, Tp*-C*H*). Some peak widths at half height could not be determined accurately due to overlapping resonances. IR = 1014 cm^{-1} (C═S), 2553, 2522 cm^{-1} (B-H).

Formation of Tp^*_2UI From Reductive Silylation. A 20 mL scintillation vial was charged with **3** (0.060 g, 0.061 mmol) and approximately 5 mL of THF. Iodotrimethylsilane (0.024 g, 0.120 mmol) was added to the solution while stirring, causing an immediate color change from dark green to bright purple. The solution was immediately dried to prevent the monoiodide species (0.052 g, 0.054 mmol, 88%) from reacting further with the silyl ester. The crude material was washed with cold pentane to separate the organic product, ($Me_3SiOC(O)CH_2Ph$), which was identified based on previously reported ^1H NMR data.[20] Infrared spectroscopy showed an absorption band at 1718 cm^{-1} assignable to the C═O of ($Me_3SiOC(O)CH_2Ph$).

Formation of Tp^*_2UCl From Reductive Silylation. A 20 mL scintillation vial was charged with **3** (0.100 g, 0.102 mmol) and approximately 5 mL of THF. Chlorotrimethylsilane (0.020 g, 0.185 mmol) was added to the solution while stirring, causing a gradual color change from dark green to blue purple over the course of 5 min. The solution was stirred for an additional 2 h before volatiles were removed in vacuo. The crude material was washed with cold pentane to separate ($Me_3SiOC(O)CH_2Ph$)[20] and unreacted starting material (22% by ^1H NMR spectroscopy). Tp^*_2UCl[14a] was isolated in a toluene washing and was recrystallized from a concentrated ether/toluene solution (0.070 g, 0.080 mmol, 78%).

Isolation and Characterization of Silyl-Ester. The silyl-ester, trimethylsilyl 2-phenylacetate, was synthesized in the reaction of chlorotrimethylsilane with **3**. Solvents were immediately removed in vacuo and the resulting solid was washed with cold pentane to separate the silyl ester. Concentration of the volatiles allowed identification of the silyl ester by ^1H NMR spectroscopy (based on a previously reported spectrum for $Me_3SiOC(O)CH_2Ph$).[20]

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Uranium(III) Alkyl, $Tp^*_2U(CH_2Ph)$ (2). Synthesis of a uranium(III) alkyl species was

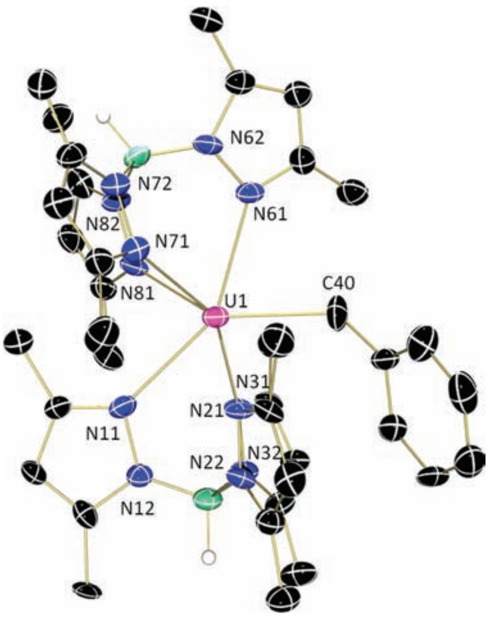


Figure 1. Molecular structure of **2** shown with 30% probability ellipsoids. Selected solvent, hydrogen, and iodine atoms omitted for clarity.

accomplished by salt metathesis of the uranium(III) monoiodide compound, **1**,[17] with 1 equiv of benzyl potassium (eq 1). After stirring and workup to remove the resulting potassium iodide, the remaining green solid (93%) was characterized by ^{1}H NMR spectroscopy (benzene-d_6), supporting formation of the desired uranium alkyl complex, **2**. Notably, the spectrum for **2** displays all of the expected peaks with the appropriate integration values, even for those protons very close to the paramagnetic uranium(III) center. As is typically observed with the bis-Tp* uranium compounds, resonances for the methyl groups pointing toward and away from the uranium center are visible at −11.10 and −2.85 ppm, respectively. The resonances for the rest of the ligand framework, including those for the pyrazole and B−H protons, are also present. Most significant is the methylene resonance, which appears at 21.35 ppm and is broadened due to its proximity to the uranium center. Broad singlet resonances for the phenyl ring range from 10.80 to 26.21 ppm. The synthesis and isolation of **2** demonstrate the stability of less sterically bulky primary alkyls as compared to those previously reported.[5,6]

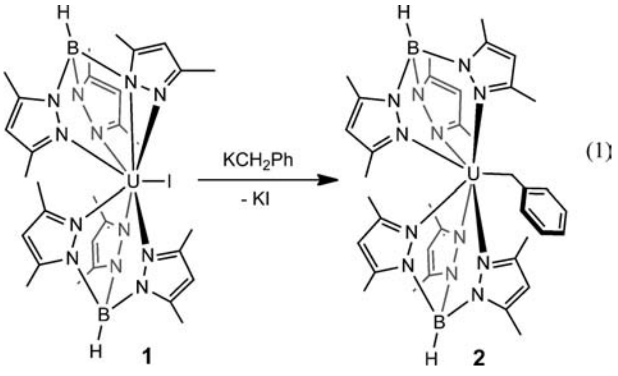
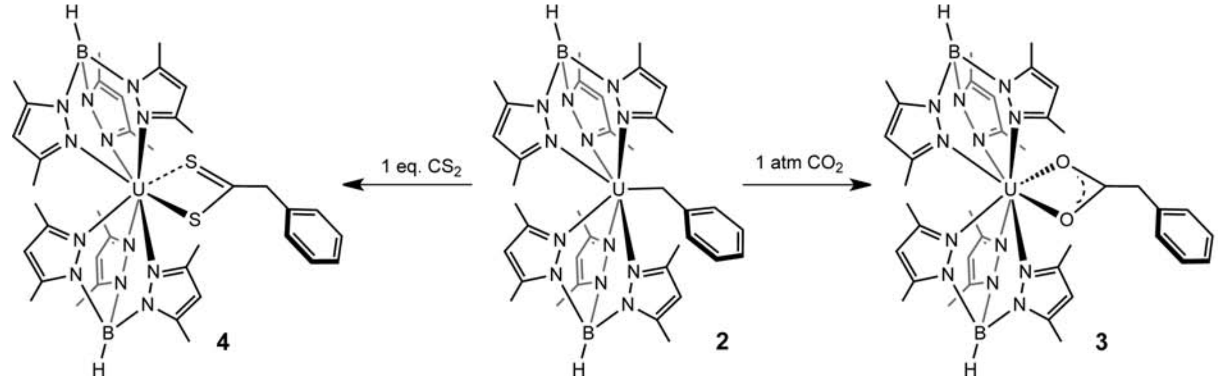


Table 1. Structural Parameters for 2, 3, and 4

	2	**3** (E = O)	**4** (E = S)
U1−N11	2.638(12) Å	2.686(7) Å	2.764(12) Å
U1−N21	2.538(10) Å	2.570(8) Å	2.540(12) Å
U1−N31	2.537(10) Å	2.645(9) Å	2.632(10) Å
U1−N61	2.734(12) Å	2.726(8) Å	2.549(10) Å
U1−N71	2.579(10) Å	2.562(7) Å	2.696(11) Å
U1−N81	2.573(10) Å	2.593(7) Å	2.692(10) Å
U1−C40	2.57(2) Å	−	−
U1−E41	−	2.490(7) Å	2.943(4) Å
U1−E42	−	2.494(7) Å	3.016(4) Å
E41−C41	−	1.228(12) Å	1.712(10) Å
E42−C41	−	1.269(13) Å	1.656(17) Å
U1−C40−C41	132.8 (14)°	−	−
E41−C41−E42	−	119.9 (9)°	122.1 (9)°
E41−U1−E42	−	51.4 (3)°	59.31 (11)°

Small green crystals of **2** were grown by cooling a THF/toluene (1:1) solution to −35 °C for further characterization by X-ray crystallography (Figure 1 and Table 1). The structure revealed a seven-coordinate uranium center with the benzyl group bonded in an η^1 fashion. In addition, a small amount of the monoiodide compound, **1**, was discovered in the crystal. The disordered fragments were refined with the constraint that the occupancies of the benzyl group and the iodine atom sum to one. Final refinement resulted in 93.3(6)% carbon and 6.7(6)% iodine. The U−C distance of 2.57(2) Å is within error of that reported for Sattelberger's uranium(III) alkyl, $U(CH(SiMe_3)_2)_3$, of 2.48(2) Å.[5b] The observed distance also compares favorably to those reported for uranium(IV) benzyl species with the same coordination mode.[21] For each Tp* ligand in **2**, two U−N distances are equal, while the third U−N bond is significantly lengthened, a common trend typically observed for bis(Tp*) uranium complexes.[14,17] The uranium−nitrogen distances for one of the ligands are 2.537(10), 2.538(10), and 2.638(12) Å, and those observed for the other ligand are 2.573(10), 2.579(10), and 2.734(12) Å. This elongation of one bond per ligand is most likely due to extreme steric hindrance at the uranium center.

Reactivity of Tp*$_2$U(CH$_2$Ph) (2) with Carbon Dioxide and Carbon Disulfide. With the uranium(III) alkyl species in hand, the chemistry with carbon dioxide and carbon disulfide was explored. Exposure of a dark-green solution of **2** to one atmosphere of carbon dioxide produced an immediate color change to bright green. Stirring for 30 min followed by removal of the volatiles in vacuo resulted in a green solid assigned as **3** in quantitative yield (eq 2). Analysis by ^{1}H NMR spectroscopy revealed a noticeable shift in all resonances as compared to **2**. Those for the methyl groups of the Tp* ligands were found at −8.76 and −0.96 ppm and are significantly broadened from those in **2**. The equivalent pyrazole and B−H protons are visible as well. The resonance assignable to the $-CH_2$ on the benzyl group appears at 17.11 ppm. Resonances for the protons on the phenyl ring are shifted upfield, ranging from 8.73 to 15.68 ppm, and now show splitting. This shifting and sharpening of the proton resonances in **3** as compared to **2** is indicative of distancing from the uranium center as would be expected from carbon dioxide insertion. An absorbance for a C═O double bond is not observable by infrared spectroscopy, indicating that the ligand is not coordinated in an η^1 fashion. Absorbances for **3** are observed at 1497 and 1491 cm^{-1}, consistent with those expected for asymmetric stretches of carbon−oxygen multiple bonds, similar to the uranium dicarboxylate species, $Cp_2U(\kappa^2\text{-}CO_2CH_2Ph)_2$, previously reported by Takats. This species



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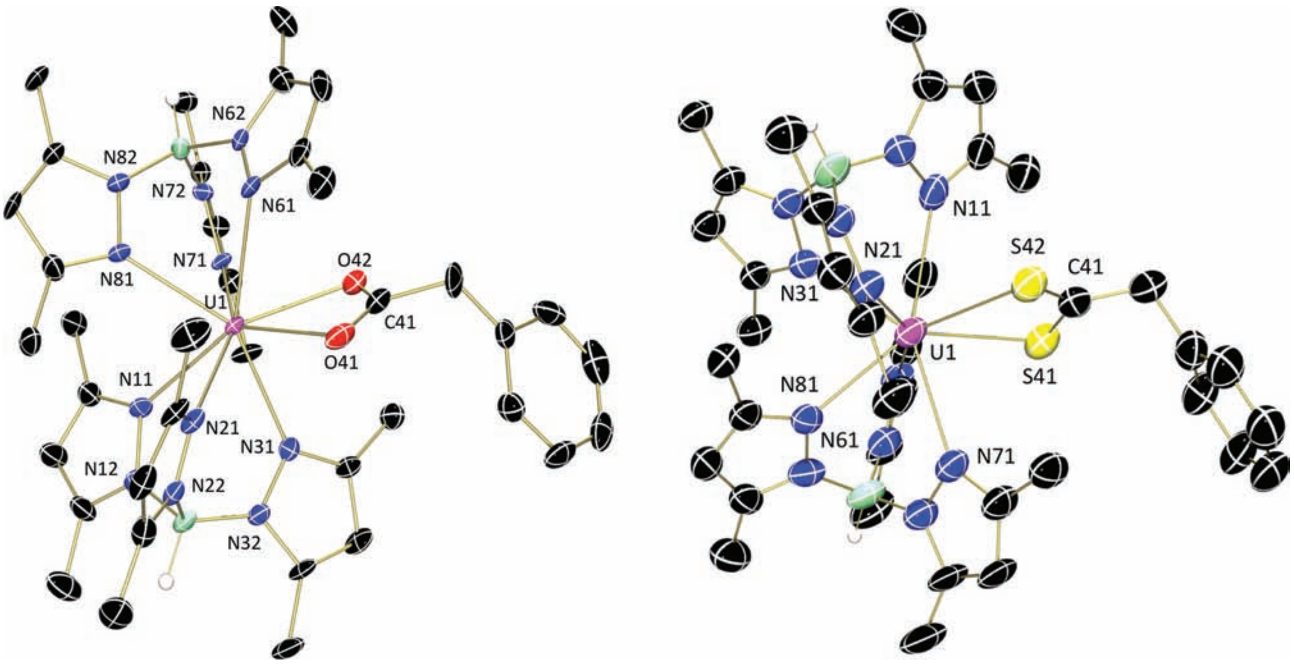


Figure 2. Molecular structure of **3** and **4** shown with 30% probability ellipsoids. Selected hydrogen atoms omitted for clarity.

displays asymmetric CO stretches at 1494 and 1488 cm^{-1}, with the corresponding symmetric stretches at 1423 cm^{-1}.[13] No symmetric stretch is visible for **3** by infrared spectroscopy as this region is obscured by ligand resonances.

As there is no previous structural characterization for a uranium(III) carboxylate, further characterization by X-ray crystallography was performed to ascertain details of the environment around the uranium (Figure 2, left). Crystals of **3** were grown at −35 °C from a concentrated THF/toluene (1:1) solution. Analysis provided confirmation of **3** as the product from insertion of carbon dioxide, Tp*$_2$U(κ^2-O$_2$CCH$_2$Ph), with an eight-coordinate uranium center featuring a bidentate carboxylate ligand.

The structural parameters for **3** are presented in Table 1. The U−N distances are similar to those observed for **2** and show the same trends. The identical U−O bond distances of 2.490(7) and 2.494(7) Å, the similar O−C bond lengths of 1.228(12) and 1.269(13) Å, and the O−C−O angle of 119.9(9)° indicate delocalization of an electron over the O−C−O fragment. These distances and angles are similar to those observed previously for uranium(VI) species with carboxylate ligands,[22] also supporting the carboxylate as a monoanionic ligand. The insertion of carbon dioxide into the uranium carbon bond marks the first example of this type of insertion at a uranium(III) center.

The observed insertion chemistry contrasts previous studies of the reductive activation of carbon dioxide reported by Meyer. Exposure of the aryloxide substituted triazacyclononane uranium(III) complexes, [((^{R}ArO)$_3$tacn)U] (R = *t*-Bu, Ad), to carbon dioxide generates interesting reduced products depending on the sterics at the uranium center. Using the sterically large adamantyl derivative results in the formation of an unprecedented charge separated radical CO$_2$ ligand coordinated in an η^1 fashion to a tetravalent uranium center.[2b] Conversely, the smaller, *tert*-butyl version of the ligand generates a bridging μ-oxo uranium(IV) dimer.[2d] Changing the ligand anchor from triazacyclononane to either a mesityl ring or a single nitrogen atom opens up the environment at the low-valent uranium center, resulting in the formation of bridging carbonate species upon addition of CO$_2$.[2c] Significantly, recent theoretical results establish that the mechanism for carbonate formation by these trivalent uranium species proceeds via insertion of carbon dioxide into tetravalent U−O bonds.[23] Similar chemistry has recently been reported by Cloke with the synthesis of the bridging carbonate species, $[((\eta\text{-C}_8\text{H}_6\text{-}\{\text{Si}^i\text{Pr}_3\text{-}1,4\}_2)(\eta\text{-C}_5\text{Me}_4\text{H})\text{U})_2(\mu\text{−}\eta^1{:}\eta^2\text{-CO}_3)]$.[24]

Similar chemistry was attempted with carbon disulfide to demonstrate the generality of the insertion reaction for the uranium−carbon bond in **2**. Layering a cold pentane solution of CS_2 on a cold THF solution of **2** followed by storage at −35 °C results in slow mixing of the layers and the precipitation of a dark-green crystalline solid assigned as **4**. Characterization by ^{1}H NMR spectroscopy showed a spectrum consistent with CS_2 insertion. Splitting is observed in the phenyl resonances due to their increased distance from the paramagnetic uranium center. These resonances are upfield shifted somewhat from those observed for **2** and **3**, ranging from 7.48 to 10.30 ppm. Compound **4** shows inequivalent methyl groups on the pyrazole rings pointing toward the uranium, suggesting a different coordination mode of the dithiocarboxylate ligand as compared to the carboxylate analogue **3**. Six resonances are observed for the methyl protons on the pyrazole rings along with the three expected peaks for the corresponding C−H protons present on those rings. A resonance for the methylene protons next to the phenyl ring is again visible at 2.27 ppm, closer to its diamagnetic reference value and sharpened due to the separation from the paramagnetic uranium center. The infrared spectrum for **4** showed an absorbance for a C=S double bond at 1014 cm^{-1}, indicating that this group is either loosely bound or not coordinated to the uranium center.

To further understand the uranium(III) dithiocarboxylate species, **4**, the molecular structure was determined by X-ray crystallography (Figure 2, right, and Table 1). Suitable crystals were grown by cooling a THF solution of **4** to −35 °C. Analysis revealed **4** as $\text{Tp*}_2\text{U(SC(S)CH}_2\text{Ph)}$ with an eight-coordinate uranium center that is structurally similar to **3**. The U−N distances are as expected and within experimental error of those reported for **2** and **3**. The U−S distances of 2.943(4) (U1−S41) and 3.016(4) Å (U1−S42) are longer than those reported for the uranium(IV) dithiocarboxylate species, $\text{Cp*}_2\text{U(S}^t\text{Bu)}(\kappa^2\text{-S}_2\text{CS}^t\text{Bu})$, which has bond distances of 2.885(4) and 2.821(5) Å.[8] The extremely long U1−S42 bond distance in **4** indicates that this is a weak, dative bond, which is supported by the inequivalency in the ^{1}H NMR spectrum and the C=S double bond character shown by infrared spectroscopy. The shorter U1−S41 distance is similar to those reported for the uranyl species $\text{UO}_2(\text{dtc})_2(\text{Ph}_3\text{AsO})$ (dtc = dithiocarbamate), $\text{UO}_2(\text{dtc})_2(\text{Ph}_3\text{PO})$, and $\text{UO}_2((\kappa^2\text{-S}_2\text{CMe})_2(\text{Ph}_3\text{PO})$.[11b,25] The C−S distances in **4** are 1.656(17) and 1.712(16) Å, similar to those observed for $\text{Cp*}_2\text{U(S}^t\text{Bu)}(\kappa^2\text{-S}_2\text{CS}^t\text{Bu})$ (1.83(2) and 1.82(2) Å)[8] and the above-mentioned uranyl analogues (range from 1.66(3) to 1.71(4) Å).[11b,25] This similarity in the bond distances supports formulation of the dithiocarboxylate ligand as a monoanionic species. The formation and characterization of **4** marks an interesting example of a uranium(III) dithiocarboxylate species as well as C−C bond formation with carbon disulfide at a low-valent uranium center.

The optical properties of **1**−**3** were examined by electronic absorption spectroscopy to establish the trivalent oxidation state of these complexes (Figure 3). Data for the dark-purple monoiodide species, **1**, and the green alkyl derivatives, **2** and **3**, were recorded in THF over 300−2000 nm. Due to the instability of **4** in solution, an electronic absorption spectrum on a pure sample was not obtainable. Low to mid intensity absorption bands, consistent with those previously observed for trivalent uranium, are distributed over 300−1300 nm.[26] For **1**, there is a shoulder in the near UV region at 361 nm (ε = ∼1000 M^{-1}cm^{-1}) and additional sharp charge-transfer bands at 564 (ε = ∼800 M^{-1}cm^{-1}) and 748 nm (ε = ∼500 M^{-1}cm^{-1}). Compound **2** displays a sharp, color-producing band at 506 (ε = ∼1000 M^{-1}cm^{-1}) and other parity allowed transitions typical of uranium(III). The electronic absorption spectrum of compound **3** features a shoulder at 429 (ε = ∼400 M^{-1}cm^{-1}) and an absorption band at 767 nm (ε = ∼300 M^{-1}cm^{-1}). Additionally, there are weak *f*−*f* transitions present throughout the near-infrared region of the spectrum for all of the compounds. The intensity and distribution of these transitions and the similarity in spectra of **2** and **3** to **1** confirms these compounds are trivalent, as the oxidation state of the latter has been established.[17] The crystallographic bond distances and similar spectroscopic properties support **4** as a trivalent uranium species as well.

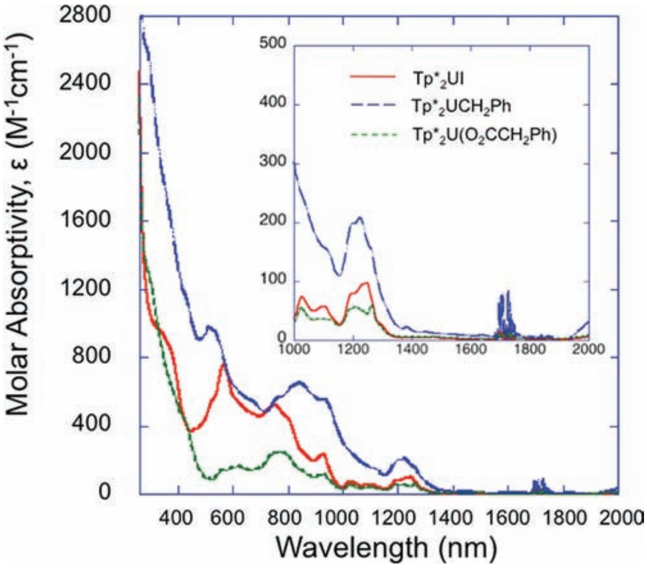
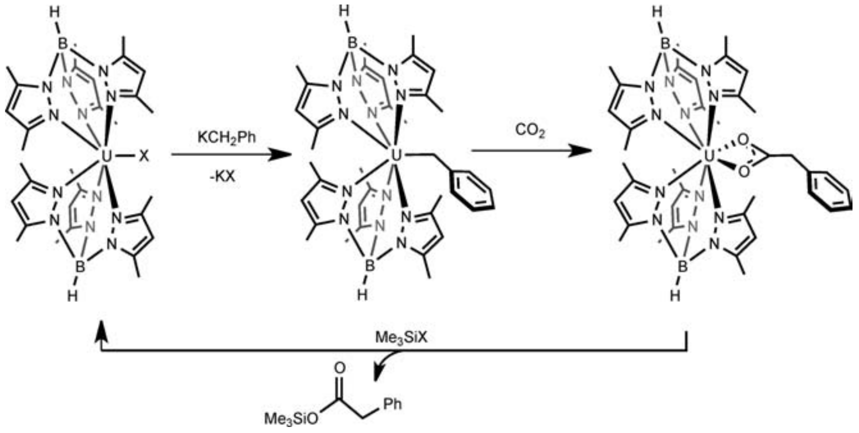


Figure 3. Electronic absorption spectra of **1**−**3** in THF at ambient temperature. Inset shows the near-infrared region of the spectrum. Solvent overtones are present in between 1600 and 1800 nm.

Reactivity of $\text{Tp*}_2\text{U}(\kappa^2\text{-O}_2\text{CCH}_2\text{Ph})$ (3) and $\text{Tp*}_2\text{U(SC(S)CH}_2\text{Ph)}$ (4). Further functionalization of the carboxylate ligand in **3** was attempted by U−O bond cleavage. Previous studies have demonstrated that the strong U−O double bonds in the uranyl cation $[\text{UO}_2^{\,2+}]$ can be broken using Si−O bond formation as a driving force,[27] but to our knowledge, this has not been used for single bonds with the aim of productive release of an organic ester from a low-valent uranium center. Addition of 1 equiv of iodotrimethylsilane to a green solution of **3** produced an immediate color change to purple, signifying formation of the uranium monoiodide species, **1**. Analysis by ^{1}H NMR spectroscopy confirmed regeneration of **1** and the formation of the silyl ester derived from CO_2, $\text{Me}_3\text{SiOC(O)CH}_2\text{Ph}$, in near quantitative yield. This ester was further characterized by infrared spectroscopy, which showed an absorption at 1718 cm^{-1} assignable to the C=O double bond. Similar chemistry was also possible with chlorotrimethylsilane, which produced the same ester and the previously reported monochloride compound, $\text{Tp*}_2\text{UCl}$.[14a] Regeneration of the starting monohalide complex allows completion of a stoichiometric cycle where carbon dioxide is functionalized on a low-valent uranium center (Scheme 1). Further studies have shown that additional benzyl potassium can be added to the regenerated **1** under an atmosphere of carbon dioxide followed by

Scheme 1. Functionalization of Carbon Dioxide



Me_3SiI to keep producing the silyl ester over at least three cycles. The ability to cleave the uranium—oxygen single bond for functionalization of the carboxylate ligand to produce the silyl ester is significant given the oxophilicity of uranium. The silyl halides used react quickly and cleanly, offering a convenient method for uranium—oxygen single-bond cleavage.

Despite attempts, the addition of trimethylsilylhalides to a freshly prepared solution of **4** did not regenerate the monohalide species to produce the silylthioester. Instead, addition of these reagents resulted in decomposition of the uranium compound, **4**, without consumption of the trimethylsilylhalide reagent, as judged by ^1H NMR spectroscopy. Other attempts at functionalization were made with benzylbromide and methyl iodide, as well as various Grignard reagents and $(PPh_3)AuCl$, but no tractable products were obtainable from these reactions, indicating there is much to learn about the stability and reactivity of U—S bonds.

CONCLUSIONS

In summary, the synthesis and characterization of a rare uranium(III) monoalkyl species by salt metathesis from the corresponding uranium monoiodide has been reported. Exposure to small amounts of carbon dioxide or an equivalent of carbon disulfide results in U—C insertion, converting the alkyl into a carboxylate or dithiocarboxylate ligand, respectively. In the case of carbon dioxide, the resulting carboxylate ligand of $Tp^*_2U(\kappa^2\text{-}O_2CCH_2Ph)$ can be liberated from the uranium center by addition of silylhalides. This process regenerates the starting monohalide complex, which can then be alkylated to repeat the cycle at least three times. The product resulting from CS_2 insertion, $Tp^*_2U(SC(S)CH_2Ph)$, was less stable in solution, and thus functionalization of the dithiocarboxylate ligand was not achieved. This work demonstrates a rare example of C—C bond formation involving a uranium(III) alkyl as well as complete scission of the uranium oxygen bond to release the silyl ester. This CO_2 and CS_2 insertion contrasts previous studies with trivalent uranium that have shown reduction of the carbon—oxygen[2b] and carbon—sulfur[12] bonds but with no functionalization or release from the uranium center. Future studies are underway to examine the scope of the CO_2 insertion and applications toward small molecule activation.

ASSOCIATED CONTENT

Supporting Information. ^1H NMR spectra, cifs, and crystallographic experimental parameters for **2**—**4**. This information is available free of charge via the Internet at http://pubs.acs.org.

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