ORGANOMETALLICS

Formation of Trivalent U-C, U-N, and U-S Bonds and Their **Reactivity toward Carbon Dioxide and Acetone**

Ellen M. Matson, Phillip E. Fanwick, and Suzanne C. Bart*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT:



A family of uranium(III) complexes of the form Tp_2^*UX ($Tp^* = hydrotris(3,5-dimethylpyrazolyl)$ borate, X = CCPh (2-CCPh), CCSiMe₃ (3-CCSiMe₃), NHPh (4-NHPh), NHCH₂Ph (5-NHCH₂Ph), SPh (6-SPh)) have been synthesized in quantitative yields by protonation of the benzyl group Tp*2U(CH2Ph) (1-CH2Ph) with organic precursors. Full characterization of these complexes, which contain newly formed uranium-carbon, uranium-nitrogen, and uranium-sulfur bonds, was performed using ¹H NMR and IR spectroscopies. These data along with the structural parameters of the uranium acetylide (2-CCPh) and uranium thiolate (6-SPh) species are reported. Treating the trivalent uranium acetylides and amides with 1 atm of carbon dioxide results in its insertion into the uranium – element bond to form the corresponding carboxylate or carbamate moiety in quantitative isolable yields. Reversible insertion of carbon dioxide (1 atm) into the uranium-sulfur bond of $Tp_2^*U(SPh)$ (6-SPh) was also noted. The new family of CO_2 -inserted uranium(III) derivatives $Tp_2^*UO_2CX$ (X = CCPh (7- O_2CCCPh), CCSiMe₃ (8- $O_2CCCSiMe_3$), NHPh (9-O₂CNHPh), NHCH₂Ph (10-O₂CNHCH₂Ph), SPh (11-O₂CSPh)) has been characterized spectroscopically and, in the case of 7- O_2CCCPh , crystallographically. The newly formed U-O bonds were cleaved by addition of trimethylsilyl halides, generating the monohalide derivative. Attempts to insert acetone into the uranium-carbon bonds of 1-CH2Ph and 2-CCPh or the uranium-nitrogen bond in 4-NHPh resulted exclusively in protonation of the benzyl ligand and isomerization to form a rare enolate complex Tp*2U(OC(CH₃)CH₂) (12-OC(CH₃)CH₂). This complex has been fully characterized by ¹H NMR and infrared spectroscopies as well as X-ray crystallography.

■ INTRODUCTION

Insertion of carbon dioxide and other carbonyl-containing substrates into metal-element bonds is a key step in many important transition-metal-mediated organic transformations,¹⁻³ and actinides undergo similar reactivity. Insertion of carbon dioxide has been noted for tetravalent uranium-carbon bonds, such as the uranium dimethyl complex $Cp_2^*UMe_2$ ($Cp^* = 1,2,3,4,5$ pentamethylcyclopentadienyl), which forms the corresponding di(acetate) $Cp_{2}^{*}U(\kappa^{2}-O_{2}CMe)$ upon exposure to low pressures of CO₂.⁴ Similarly, the uranium bis(acetylide) Cp*₂U(CCPh)₂ forms $Cp_2^*U(\kappa^2-O_2CCCPh)$ by CO_2 insertion.⁵ Amido complexes, such as $Cp_2^*U(NEt_2)_{2,0}^6$ [((^RArO)_3tacn)U(NHMes)] $((^{R}ArO)_{3}tacn = 1,4,7-tris(3-R-5-tert-butyl-2-hydroxybenzyl)-1,4,$ 7-triazacyclononane, R = tBu, Ad),⁷ and other tetrakis(dialkylamido) uranium(IV) derivatives, yield carbamate ligands by insertion of CO₂ into the U-N bond.⁸⁻¹⁰ Although the insertion chemistry of uranium(IV) sulfido species has had less attention, U-S bonds have been shown to reversibly insert carbon dioxide and carbon disulfide.¹¹

The small size of carbon dioxide facilitates insertion chemistry, but examples of insertion using larger carbonyl-containing substrates have also been reported. Multiple ketones and aldehydes insert into the U-C bond in $((Me_3Si)_2N)_3UCH_3^{12}$ while a cyclometalated derivative of $U(N(SiMe_3)_2)_3$, $((Me_3Si)_2N)_2$ - $U(Me_3SiNSi(Me)_2CH_2)$,¹³ readily inserts the carbonyl of substituted cyclohexanones into the U-C bond to produce spirometallacycles. The ansa-thorium metallocene Me₂Si(η^5 - $C_5(CH_3)_4)_2$ Th(CH₃)₂ dimerizes aldehydes, which is proposed to proceed through insertion of the carbonyl into the Th-C bond.14

Recently, we have reported that the uranium(III) alkyl complex $Tp_2^*U(CH_2Ph)$ (1) undergoes insertion of carbon dioxide along the uranium-carbon bond, producing the rare uranium-(III) carboxylate $Tp_2^*U(\kappa^2-O_2CCH_2Ph)$.¹⁵ This insertion is immediate at ambient or low temperatures with low pressures of CO₂ (\leq 1 atm). Due to the relatively underexplored nature of

Received: July 9, 2011 Published: October 17, 2011 insertion reactions at uranium(III) centers, we set out to perform a systematic study of the insertion of carbon dioxide and acetone along trivalent uranium—element bonds, specifically sp-hybridized U—C bonds, amido U—N bonds, and thiolate U—S bonds. Herein we present the syntheses of uranium(III) species containing these moieties, as well as their reactivity toward carbon dioxide and acetone.

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.¹⁶ Benzene-d₆ 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. Phenylacetylene, ethynyltrimethylsilane, aniline, benzylamine, and benzenethiol were purchased from Sigma Aldrich, dried over CaH₂, and vacuum-distilled before use. Acetone was purchased from Sigma Aldrich, dried over CaCl₂, and vacuum-transferred before use. Carbon dioxide (99.9%, anhydrous) was purchased from Sigma Aldrich and used as received. Tp*2U(CH2Ph) was prepared according to literature procedures.13

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 299.992 MHz. All chemical shifts were reported relative to the peak for 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 Micro-Max002+ high-intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu K α radiation ($\lambda = 1.541$ 84 A). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.¹⁷ The structures were solved using the structure solution program PATTY in DIRDIFF99.¹⁸ Refinement was performed on a LINUX PC using SHELX-97.¹⁷ The data were collected at a temperature of 150(1) K.

General Procedure for Preparation of Uranium(III) Complexes by Protonation. A 20 mL scintillation vial was charged with 0.100 g (0.108 mmol) of $Tp_2^*U(CH_2Ph)$ and approximately 3 mL of tetrahydrofuran, making a dark green solution. After the sample was cooled to -35 °C, a microsyringe was used to deliver 1 equiv of an organic substrate with an acidic hydrogen (2, phenylacetylene; 3, trimethylsilylacetylene; 4, aniline; 5, benzylamine; 6 = benzenethiol) with stirring. After 5 min, the solvent and toluene (byproduct) were removed in vacuo, leaving a solid.

 $Tp_{2}U(C \equiv CPh)$ (**2-CCPh**). The product was washed with pentane to remove the byproduct toluene, leaving a blue-green crystalline solid assigned as $Tp_{2}^{*}U(C \equiv CPh)$. Yield: 0.093 g (0.100 mmol, 96%).

¹H NMR (C_6D_6 , 25 °C, ppm): -13.49 (28, 18H, Tp*-CH₃), 0.62 (7, 18H, Tp*-CH₃), 7.49 (7, 6H, Tp*-CH), 9.95 (17, 2H, phenyl-CH), 13.25, (13, 1H, *p*-phenyl-CH), 20.64 (21, 2H, phenyl-CH). IR: 2049 cm⁻¹ (C=C), 2526, 2554 cm⁻¹ (B-H). Spectroscopic data matches those previously reported by Takats.¹⁹

Tp^{*}₂*U*(*C*≡*CSiMe*₃) (**3-CCSiMe**₃). The remaining blue solid was washed with cold pentane and dried, leaving a product assigned as Tp^{*}₂*U*(*C*≡*CSiMe*₃). Yield: 0.101 g (0.107 mmol, 97%). Anal. Calcd for C₃₅H₅₃N₁₂SiB₂U: C, 45.22; H, 5.75; N, 18.01. Found: C, 45.17; H, 5.75; N, 18.03. ¹H NMR (C₆D₆, 25 °C, ppm): -13.53 (26, 18H, Tp*-CH₃), 0.69 (8, 18H, Tp*-CH₃), 7.04 (9, 9H, Si-(CH₃)₃), 7.57 (9, 6H, Tp*-CH). IR: 1997 cm⁻¹ (C≡C), 2526, 2555 cm⁻¹ (B−H).

 $Tp_{2}U(NHPh)$ (**4-NHPh**). The remaining solid was recrystallized from a pentane/ether mixture (20/1) at -35 °C, producing a blue-green crystalline solid assigned as $Tp_{2}^{*}U(NHPh)$. Yield: 0.094 g (0.102 mmol, 98%). Anal. Calcd for $C_{36}H_{50}N_{13}B_{2}U$: C, 46.77; H, 5.45; N, 19.70. Found: C, 46.51; H, 5.39; N, 19.32. ¹H NMR ($C_{6}D_{6}$, 25 °C, ppm): -10.31 (1286, 18H, Tp^{*} -CH₃), -2.33 (70, 18H, Tp^{*} -CH₃), 0.80 (278, 2H, B-H), 7.20 (55, 6H, Tp^{*} -CH), 14.43 (40, 1H, *p*-phenyl-CH), 18.84 (85, 2H, phenyl-CH), 34.89 (79, 2H, phenyl-CH), 75.02 (219, 1H, N-H). IR: 2526, 2551 cm⁻¹ (B-H), 3369 cm⁻¹ (N-H).

 $Tp^{*}_{2}U(NHCH_2Ph)$ (**5-NHCH_2Ph**). The remaining solid was recrystallized from a pentane/ether mixture (20/1), producing a brown crystalline solid assigned as $Tp^{*}_{2}U(NHCH_2Ph)$. Yield: 0.092 g (0.098 mmol, 94%). Anal. Calcd for $C_{37}H_{50}N_{13}O_2B_2U$: C, 47.35; H, 5.58; N, 19.40. Found: C, 47.04; H, 5.28; N, 19.46. ¹H NMR (C_6D_6 , 25 °C, ppm): -7.21 (63, 18H, Tp^{*} -CH₃), -3.73 (15, 18H, Tp^{*} -CH₃), 4.72 (344, 2H, B-H), 7.64 (20, 6H, Tp^{*} -CH), 12.60 (34, 1H, *p*-phenyl-CH), 14.48 (31, 2H, phenyl-CH), 28.56 (34, 2H, phenyl-CH), 97.15 (111, 2H, CH₂), 103.48 (299, 1H, N-H). IR: 2526, 2551 cm⁻¹ (B-H), 3310 cm⁻¹ (N-H).

 $Tp^{*}_{2}U(SPh)$ (**6-SPh**). The remaining dark blue solid was washed with pentane and dried, leaving a dark blue powder assigned as $Tp^{*}_{2}U(SPh)$. Yield: 0.094 g (0.100 mmol, 96%). Anal. Calcd for $C_{36}H_{49}N_{12}B_{2}SU$: C, 45.92; H, 5.25; N, 17.85. Found: C, 46.07; H, 5.28; N, 17.76. ¹H NMR ($C_{6}D_{6}$, 25 °C, ppm): -11.55 (23, 18H, $Tp^{*}-CH_{3}$), -0.53 (6, 18H, $Tp^{*}-CH_{3}$), 5.61 (178, 2H, B-H), 7.49 (6, 6H, $Tp^{*}-CH$), 11.21 (18, 1H, phenyl-CH), 13.47 (18, 2H, phenyl-CH), 20.89 (30, 2H, phenyl-CH). IR: 2521, 2548 cm⁻¹ B-H.

General Procedure for Preparation of CO_2 -Inserted Complexes (7–10). In a glovebox, a THF solution of 0.100 g of the appropriate uranium(III) precursor was added into a thick-walled glass vessel and sealed. On the Schlenk line, the sample was frozen with liquid nitrogen and the head space of the flask evacuated. After the sample was warmed to room temperature under vacuum, 1 atm of CO_2 was added to the flask with stirring. Reaction progress was monitored by color change of the sample and uptake of CO_2 as measured by the manometer. All reactions proceeded immediately on the basis of the color change. However, stirring was continued for an additional 30 min to ensure conversion. Solvent was then removed in vacuo.

 $Tp_{2}^{*}U(\kappa^{2}-O_{2}CCCPh)$ (**7**-*O***₂***CCCPh***). A dark green powder assigned as Tp_{2}^{*}U(\kappa^{2}-O_{2}CC\equiv CPh) was isolated in quantitative yield, with no further purification necessary (0.104 g, 0.106 mmol, 98%). Anal. Calcd for C_{39}H_{49}N_{12}O_{2}B_{2}U: C, 47.92; H, 5.05; N, 17.19. Found: C, 48.66; H, 5.38; N, 16.44. ¹H NMR (C_{6}D_{6}, 25 °C, ppm): -9.23 (134, 18H, Tp^{*}-CH₃), -0.31 (5, 18H, Tp^{*}-CH₃), 2.77 (339, 2H, B-H), 7.39 (9, 6H, Tp^{*}-CH), 8.15 (t,** *J* **= 7.2 Hz, 2H, phenyl-CH), 8.84 (t,** *J* **= 7.8 Hz, 1H,** *p***-phenyl-CH), 11.46 (d,** *J* **= 7.2 Hz, 2H, phenyl-CH). IR: 2211 cm⁻¹ (C\equivC); 2522, 2551 cm⁻¹ (B-H).**

 $Tp_{2}^{*}U(\kappa^{2}-O_{2}CCCSiMe_{3})$ (8- $O_{2}CCCSiMe_{3}$). A green powder was recovered with no purification necessary and assigned as $Tp_{2}^{*}U(\kappa^{2}-O_{2}CC\equiv CSiMe_{3})$ (0.100 g, 0.103 mmol, 99%). Anal. Calcd for $C_{36}H_{53}N_{12}O_{2}B_{2}SiU$: C, 44.41; H, 5.49; N, 17.26. Found: C, 44.38; H, 5.54; N, 17.16. ¹H NMR ($C_{6}D_{6}$, 25 °C, ppm): -9.14 (132, 18H,

	2-CCPh	3-CCSiMe ₃	4-NHPh	5-NHCH ₂ Ph	6-SPh
Tp*-CH ₃	-13.49, 0.62	-13.53, 0.69	-10.31, -2.33	-7.21, -3.73	-11.55, -1.53
Тр*-СН	7.49	7.57	7.20	7.64	7.49
B-H	а	а	0.80	4.72	5.61
<i>p</i> -phenyl	9.95	-	14.43	12.60	11.21
<i>m</i> -phenyl	13.25	-	18.84	14.48	13.47
o-phenyl	20.64	-	34.89	28.56	20.89
N-H	_	-	75.02	103.48	_
Si(CH ₃) ₃	_	7.04	-	_	_
CH ₂	_	-	-	97.15	_
^{<i>a</i>} Covered by peak i	for Tp*-CH.				

Table 1. Π MMR Data (ppm) for 2-CCPh, 5-CCSIMe ₃ , 4-MHPh, 5-MHCH ₂ Ph, and 0-SPh Measured in Denzene- u_6 at 2	Table 1.	. ¹ H NMR Data (ppn	n) for 2-CCPh, 3-CCSiMe	3, 4-NHPh, 5-NHCH ₂ Ph,	, and 6-SPh Measured in Benzer	ne- <i>d</i> ₆ at 25	°C
---	----------	--------------------------------	-------------------------	------------------------------------	--------------------------------	---------------------------------	----

Tp*-CH₃), −0.34 (13, 18H, Tp*-CH₃), 0.63 (304, 2H, BH), 2.34 (10, 9H, Si-(CH₃)₃), 7.38 (23, 6H, Tp*-CH). IR: 2185 cm⁻¹ (C≡C); 2524, 2558 cm⁻¹ (B−H).

 $Tp_{2}^{*}U(\kappa^{2}-O_{2}CNHPh)$ (**9-O₂CNHPh**). A green powder assigned as $Tp_{2}^{*}U(\kappa^{2}-O_{2}CNHPh)$ was isolated in quantitative yield after washing with pentane (0.104 g, 0.103 mmol, 99%). Anal. Calcd for $C_{37}H_{50}N_{13}O_{2}B_{2}U$: C, 45.54; H, 5.20; N, 18.80. Found: C, 45.54; H, 4.90; N, 18.59. ¹H NMR ($C_{6}D_{6}$, 25 °C, ppm): -9.64 (499, 18H, $Tp^{*}-CH_{3}$), -0.01 (22, 18H, $Tp^{*}-CH_{3}$), 3.38 (271 2H, B-H), 7.50 (22, 6H, $Tp^{*}-CH$), 9.17 (22, 1H, *p*-phenyl-CH), 9.87 (23, 2H, phenyl-CH), 16.92 (24, 2H, phenyl-CH), 28.51 (25, 1H, NH). IR: 2522, 2552 cm⁻¹ (B-H), 3279 cm⁻¹ (N-H).

 $Tp^{*}_{2}U(\kappa^{2}-O_{2}CNHCH_{2}Ph) (10-O_{2}CNHCH_{2}Ph). A green powder isolated in quantitative yield after washing with pentane (0.105 g, 0.103 mmol, 99%) was assigned as Tp^{*}_{2}U(\kappa^{2}-O_{2}CNHCH_{2}Ph). Anal. Calcd for C_{38}H_{52}N_{13}O_{2}B_{2}U: C, 46.45; H, 5.33; N, 18.53. Found: C, 46.37; H, 5.22; N, 18.11. ¹H NMR (C_{6}D_{6}, 25 °C, ppm): -9.46 (389, 18H, Tp^*-CH_{3}), -0.49 (8, 18H, Tp^*-CH_{3}), 2.60 (280, 2H, B-H), 7.14 (9, 6H, Tp^*-CH), 8.41 (t, J = 7.5, 2H, phenyl-CH), 8.97 (t, J = 8.1, phenyl-CH), 13.11 (d, J = 6.9, phenyl-CH), 15.12 (14, 2H, CH_{2}), 26.83 (29, 1H, N-H). IR: 2527, 2550 cm⁻¹ (B-H), 3277 cm⁻¹ (N-H).$

 $Tp_{2}^{*}U(\kappa^{2}-O_{2}CSPh)$ (**11-O₂CSPh**). A J. Young NMR tube was charged with 0.010 g (0.011 mmol) of $Tp_{2}^{*}U(SPh)$ (**6-SPh**) and a minimal amount of benzene- d_{6} , producing a dark blue solution. On the Schlenk line, the solution was frozen with liquid nitrogen and the head space evacuated, followed by warming to room temperature. One atmosphere of CO₂ was added to the tube, resulting in an immediate color change from dark blue to bright green. Due to the reversibility of the reaction, $Tp_{2}^{*}U(\kappa^{2}-O_{2}CSPh)$ could not be isolated in the solid state. ¹H NMR (C₆D₆, 25 °C, ppm): -9.51 (42, 18H, Tp^*-CH₃), -0.22 (6, 18H, Tp^*-CH₃), 2.88 (143, 2H, B-H), 7.37 (6, 6H, Tp^*-CH), 8.50 (17, 1H, *p*-phenyl-CH), 8.94 (18, 2H, phenyl-CH), 13.72 (17, 2H, phenyl-CH).

 $Tp_{2}UOC(CH_{3})CH_{2}$ (**12-OC(CH_{3})CH_{2}**). A solution of 0.100 g (0.108 mmol) of $Tp_{2}^{*}UCH_{2}Ph$ (**1-CH_{2}Ph**) was dissolved in approximately 3 mL of THF and cooled to -35 °C. After this time, 1 equiv of acetone (0.008 mL, 0.108 mmol) was added to the dark green solution via microsyringe. The solution immediately changed from green to brown. Volatiles were removed in vacuo, leaving a brown oil. Extraction of the product with pentane and crystallization at -35 °C over 2 days afforded a brown solid (0.072 g, 0.081 mmol, 76%). Small, brown, X-ray-quality crystals were grown from a concentrated solution of pentane and toluene (8/2 ratio). Anal. Calcd: C, 44.56; H, 5.55; N, 18.89. Found: C, 44.73; H, 5.49; N, 18.88. ¹H NMR (C₆D₆, 25 °C, ppm): -12.66 (28, 18H, $Tp^{*}-CH_{3}$), -1.11 (4, 18H, $Tp^{*}-CH_{3}$), 4.16 (183, 2H, B-H), 7.09 (5, 6H, $Tp^{*}-CH_{3}$). IR: 2528, 2555 cm⁻¹ (B-H).

General Procedure for Reductive Silylation. A 20 mL scintillation vial was charged with 0.100 g of the CO₂ -inserted product (7-O₂CCCPh, 0.102 mmol; $8-O_2CCCSiMe_3$, 0.103 mmol; 9-O₂CNHPh, 0.103 mmol; 10-O₂CNHCH₂Ph, 0.101 mmol) and approximately 5 mL of THF. One equivalent of TMSX (X = Cl, I) was added to the solution via microsyringe. Within 5 min the solution had changed to dark blue-purple, indicating the formation of the monohalide species (7-O₂CCCPh, TMSCl 0.054 g, 0.063 mmol, 62%; TMSI 0.064 g, 0.067 mmol, 66%; $8-O_2CCCSiMe_3$, TMSCl 0.051 g, 0.059 mmol, 57%, TMSI 0.070 g, 0.073 mmol, 71%; 9-O₂CNHPh, TMSCl 0.084 g, 0.084 mmol, 91%; 10-O₂CNHCH₂Ph, TMSI 0.084 g, 0.084 mmol, 83%, TMSCl 0.084 g, 0.087 mmol, 86%).

RESULTS AND DISCUSSION

Synthesis and Characterization of Uranium(III) Organometallic Complexes. To study the formation of uranium(III) acetylide, amide, and thiolate complexes, a general procedure was developed for their synthesis. Treating $Tp_2^*U(CH_2Ph)$ (1- CH_2Ph) with an organic reagent containing an acidic hydrogen $(pK_a \le 25)$ results in protonation of the benzyl group and formation of the desired uranium(III) complexes in quantitative yields (eq 1). In each case, toluene was formed as confirmed by ¹H NMR spectroscopy, signifying procession of the reaction.



These uranium(III) derivatives show similar trends by ¹H NMR spectroscopy (Table 1). For all derivatives, there are two resonances for the sets of methyl peaks that point toward and away from the uranium center. Those that point toward the uranium center are shifted drastically, ranging from -14 to -7 ppm. Those directed away from the uranium center are closer to their expected diamagnetic reference values, located from -4 to 1 ppm. The resonance for the equivalent C–H peak on the pyrazole rings appear between 7 and 8 ppm for all compounds.

Table 2. Absorption Bands Measured by Infrared Spectroscopy (cm^{-1}) for Complexes 2-CCPh, 3-CCSiMe₃, 4-NHPh, 5-NHCH₂Ph, and 6-SPh (KBr)

	В-Н	C≡C	N-H
2-CCPh	2526, 2554	2049	_
3-CCSiMe ₃	2526, 2555	1997	_
4-NHPh	2525, 2554	_	3369
5-NHCH ₂ Ph	2526, 2551	_	3305
6-SPh	2521, 2548	-	_

A broad singlet is visible for the B–H moieties at variable positions, depending on the substitution at the uranium. Infrared spectroscopy shows two inequivalent absorptions for the B–H in the solid state (Table 2); for U(III) acetylide, amide, and thiolate compounds, one absorption is observed in the range of 2520–2526 cm⁻¹, while the second appears from 2548 to 2555 cm⁻¹.

Treating 1-CH₂Ph with phenylacetylene or ethynyltrimethylsilane produces the trivalent uranium acetylides Tp*2U- $(C \equiv CPh)$ (2-CCPh) and $Tp^*_2U(C \equiv CSiMe_3)$ (3-CCSiMe_3). 2-CCPh was previously synthesized by Takats via amide protonation, and characterization of 2-CCPh by ¹H NMR and infrared spectroscopy (KBr) at 25 °C matches previously reported data (Tables 1 and 2).¹⁹ Characterization of 3-CCSiMe₃ by ¹H NMR spectroscopy (benzene- d_6) revealed spectroscopic features similar to those of 2-CCPh. The resonance for the trimethylsilyl group appears at 7.04 ppm and is shifted significantly, due to proximity to the paramagnetic uranium center. Infrared absorption bands for the carbon-carbon triple bonds in 2-CCPh and 3-CCSiMe₃ appear at 2049 and 1997 cm⁻ respectively, indicating that this bond has been slightly reduced upon coordination to the uranium center as compared to free phenylacetylene (2110 cm⁻¹) and (trimethylsilyl)acetylene (2034 cm^{-1}) . To our knowledge, uranium(III) acetylide species are rare,²⁰ but the infrared spectroscopic data for **2-CCPh** and 3-CCSiMe3 are consistent with those reported for the C=C bond in similar tetravalent uranium species, including $Cp_{2}^{*}U(CCPh)_{2}(2056 \text{ cm}^{-1}),^{21}Cp_{2}^{*}UCCPh(NPh_{2})(2062 \text{ cm}^{-1}),$ $Cp_{2}^{*}UCC$ -p-MeC₆H₄(NPh₂)(2059 \text{ cm}^{-1}),^{22}[N_{3}N]UCCPh (2052 cm^{-1}) ,²³ and $[N_3N]$ UCC-*o*-Me-C₆H₄ (2050 cm⁻¹) $([N_3N] = [(RNCH_2CH_2)_3N)]_3^{2-}; R = SiMe_2^{t}Bu).^{23}$

In a similar fashion, bis(Tp*) uranium(III) amide complexes are synthesized by addition of 1 equiv of aniline or benzylamine to **1-CH₂Ph.** Washing with pentane affords clean $Tp_2^*U(NHPh)$ (4-NHPh) as a blue-green powder, while isolation of pure Tp_2^*U -(NHCH₂Ph) (5-NHCH₂Ph) was accomplished by recrystallization, producing a dark brown solid. Characterization by ¹H NMR spectroscopy shows all of the expected resonances for 4-NHPh (Table 1). In addition to those for the ligand, the para, meta, and ortho protons for the phenyl rings in both 4-NHPh and 5-NHCH₂Ph show a characteristic pattern, with ortho being the most downfield. The resonances for the NH functionality are shifted far downfield to 75.02 and 103.48 ppm, respectively, and are significantly broadened due to proximity to the metal center. Although they are close to the uranium center, protons of the CH₂ are also visible. These uranium(III) amide complexes are unique, given the proximity of the N-H bond to the electron-rich uranium center. Confirmation of the presence of the N-H was obtained by IR spectroscopy for both molecules, which have broad absorptions at 3369 cm⁻¹ (4-NHPh) and 3305 cm⁻¹ (5-NHCH₂Ph), and are reduced from the values in the free amines (Table 2).

Previous examples of homoleptic uranium(III) amides include $U(N(SiMe_3)_2)_3$ reported by Andersen,²⁴ and more recently, convenient synthetic methodologies for $U(N(SiMe_2Ph)_2)_3$,²⁵ $U(THF)(N[R]Ar)_3$ (R = tBu, Ar = 3,5-Me_2C_6H_3),²⁶ and $[K(THF)_2]_2[U(NH-2,6-i-Pr_2C_6H_3)_5]) \cdot THF^{27}$ have been developed. Heteroleptic examples of uranium(III) amides are common,²⁸⁻³⁰ with examples similar to the system reported here being $Tp^*_2UNR_2$ (R = Ph, SiMe_3),³¹ $Tp^*U(N(SiMe_3)_2)_2$,³² and $Cp^*_2UN(SiMe_3)_2$,³³

The synthesis of a uranium(III) thiolate species was performed by treating **1-CH₂Ph** with benzenethiol, causing an immediate color change from green to dark blue. From this reaction, a dark blue-gray solid assigned as $Tp^*_2U(SPh)$ (**6-SPh**) was isolated in quantitative yield after washing. Characterization by ¹H NMR spectroscopy showed phenyl protons downfield with chemical shifts of 11.2, 13.5, and 20.9 ppm (Table 1) along with those previously discussed for the ligand. Trivalent uranium thiolates are rare; Ephritikhine has isolated the trivalent uranium thiolate anions $[Cp^*_2U(S^iPr)_2]^{-34}$ and $[Cp^*_2U(dddt)]^-$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate),³⁵ as well as the neutral homoleptic U(SMes^{*})₃ (Mes^{*} = 2,4,6-tri-*tert*-butylphenyl).³⁶ Unlike U(SMes^{*})₃, which decomposes above -25 °C in the solid state, **6-SPh** is stable at room temperature.

As demonstrated here, protonation of $Tp^*_2UCH_2Ph$ with commercially available organic substrates is a convenient entry into a variety of uranium(III) species with a wide range of steric and electronic properties. Further, this method is synthetically easy to perform, yields products in near-quantitative conversion in extremely short reaction times, and leaves toluene as the only byproduct, which can be easily removed under vacuum. This procedure eliminates the need for producing alkali-metal salts of the organic reagents, which can be difficult for reagents with functional groups and requires longer reaction times for full conversion to the organouranium complex.

Due to the limited amount of structural data on uranium(III) acetylide and thiolate compounds, 2-CCPh and 6-SPh were further characterized by single-crystal X-ray crystallography (Figure 1 and Table 3). Green block crystals of 2-CCPh suitable for analysis were grown from a concentrated THF/toluene (2/1)solution at -35 °C, and analysis confirmed the identity of the product as Tp*₂U(CCPh), which features a seven-coordinate uranium center with a linear acetylide ligand. Four of the U-N distances for Tp* range from 2.544(6) to 2.621(6) Å, while one U–N bond in each ligand is significantly longer at 2.656(5) and 2.680(5) Å. This is typically observed for uranium complexes with the bis(hydrotris(3,5-dimethylpyazolyl)borate) ligand framework.^{37,38} The uranium-carbon bond distance is 2.589(9) Å, slightly longer than what has been typically observed for uranium(IV) acetylides, which range from 2.339 to 2.468 Å, and is consistent with coordination to a more electron-rich uranium center. In addition, the C≡C triple bond in 2-CCPh is 1.100(11) Å, shorter than carbon-carbon triple bonds observed for uranium(IV) species (1.150–1.289 Å). $^{22,39-42}$ This shortening of the carbon-carbon triple bond in the crystal structure of 2-CCPh has also been observed for Cp*2SmCCPh-(THF).⁴³ Finally, the U–C–C angle in $Tp_2^*U(CCPh)$ $(177.7(8)^{\circ})$ is the closest to linearity reported for all of the uranium acetylide compounds to date. Compound 2-CCPh is isostructural with the previously synthesized and crystallographically characterized samarium compound Tp*₂Sm(CCPh), which features a C \equiv C distance of 1.206(12) Å and an Sm-C-C angle of 176.6(8)°.



Figure 1. Molecular structures of 2-CCPh (right) and 6-SPh (left) shown with 30% ellipsoids. Selected hydrogen atoms and cocrystallized solvents are omitted for clarity.

Table 3.	Structural Parameters ((Distances in A	and Angles in
deg) for	2-CCPh and 6-SPh		-

	2-CCPh	6-SPh
U1-N11	2.656(5)	2.670(5)
U1-N21	2.558(6)	2.566(5)
U1-N31	2.621(6)	2.496(4)
U1-N61	2.680(5)	2.674(5)
U1-N71	2.544(6)	2.571(5)
U1-N81	2.601(6)	2.586(5)
U1-C41	2.589(9)	_
C41-C42	1.100(11)	_
U1-S40	_	2.857(15)
U1-C41-C42	177.7(8)	_
U1-S40-C41	_	113.8(2)

The identity of 6-SPh was confirmed by X-ray diffraction, with suitable crystals grown from a concentrated THF/toluene (3/1)solution. Analysis showed the expected seven-coordinate uranium(III) η^1 -thiolate species Tp*₂USPh (Figure 1, Table 3). The U–N distances for the hydro(trispyrazolyl)borate ligands are consistent with those previously observed for 2-CCPh and other bis(ligand) derivatives.^{19,37,38} The U–S distance in **6-SPh** of 2.857(15) Å is similar to the U–S distances in the uranium(III) anions $[Cp_{2}^{*}U(S^{i}Pr)_{2}]^{-}$ (2.78(1) Å)³⁴ and $[Cp_{2}^{*}U(dddt)]^{-}$ $(2.773(7)^{\circ}A)^{.35}$ In comparison, U(SMes^{*})₃ has three thiolate ligands in an η^3 bonding mode, which gives rise to a shorter average U-S distance of 2.720(5) Å and U-S-C angle of 81.6°. The same angle for the η^1 -thiolate ligand in **6-SPh** is $113.8(2)^{\circ}$; thus, the differences in the structural parameters can be attributed to the different hapticities of the thiolate ligands. The U-S-C angles for 6-SPh are more appropriately compared to those of tetravalent η^1 derivatives, such as U(SPh)₄-(pyridine)₃.⁴⁴ This molecule features a sterically crowded sevencoordinate uranium center that does not have open sites for η^3 coordination of the thiolate group. On average, the U-S

distance reported for **6-SPh** is longer than those reported for uranium(IV) thiolate complexes with η^1 coordination (2.68–2.75 Å),^{44–47} as would be expected on the basis of the larger atomic radius of uranium(III) as compared to uranium(IV).

Carbon Dioxide Insertion Chemistry. The insertion chemistry of the trivalent U–C, U–N, and U–S bonds was explored with carbon dioxide. Exposing 2-CCPh, 3-CCSiMe₃, 4-NHPh, 5-NHCH₂Ph, and 6-SPh to 1 atm of CO₂ produces immediate color changes to green for all reactions, forming the corresponding uranium(III) carboxylate derivatives $Tp^*_2U(\kappa^2-O_2CCCPh)$ (7-O₂CCCPh) and $Tp^*_2U(\kappa^2-O_2CCCSiMe_3)$ (8-O₂CCCSiMe₃), the carbamate derivatives $Tp^*_2U(\kappa^2-O_2CNHPh)$ (9-O₂CNHPh) and $Tp^*_2U(\kappa^2-O_2CNHCH_2Ph)$ (10-O₂CNHCH₂Ph) (eq 2), and the carboxylate $Tp^*_2U(\kappa^2-O_2CSPh)$ (11-O₂CSPh) (eq 3).



Analysis of the products from the reactions with carbon dioxide by ¹H NMR spectroscopy (benzene- d_6 , Table 4) showed similar features for the entire family of compounds. The increase in the distance between the paramagnetic uranium(III) center and the seventh ligand that results from insertion of carbon dioxide into the uranium–element bond causes a shifting of the resonances for the carboxylate substituent toward their diamagnetic reference values. Resonances for the methyl groups of the hydrotris(pyrazolyl)borate ligands appear between -9 and -10 ppm and between 0 and -0.5 ppm, while those assignable to the pyrazole C–H are found in the range of 7–8 ppm. A broad singlet for the B-H is present between 2 and 4 ppm. For those species with phenyl groups, these resonances appear

	7-O ₂ CCCPh	8-O ₂ CCCSiMe ₃	9-O ₂ CNHPh	10-O ₂ CNHCH ₂ Ph	11-O ₂ CSPh
Tp*-CH ₃	-9.23, -0.31	-9.14, -0.34	-9.64, -0.01	-9.46, -0.49	-9.51, -0.22
Tp*-CH	7.39	7.38	7.50	7.14	7.37
B-H	2.75	а	3.38	2.60	2.88
<i>p</i> -phenyl	8.15	_	9.17	8.41	8.50
<i>m</i> -phenyl	8.84	_	9.87	8.97	8.94
o-phenyl	11.46	_	16.92	13.11	13.72
N-H	_	_	28.51	26.83	_
Si(CH ₃) ₃	_	2.34	_	_	_
CH ₂	_	_	_	15.12	_
^{<i>a</i>} Obscured by the S	Si(CH ₃) ₃ peak.				

Table 4. ¹H NMR Data for CO₂-Inserted Compounds 7-O₂CCCPh, 8-O₂CCCSiMe₃, 9-O₂CNHPh, 10-O₂CNHCH₂Ph, and 11-O₂CSPh Measured in Benzene- d_6 at 25 °C

Table 5. Absorption Bands (cm^{-1}) As Measured by Infrared Spectroscopy for Complexes 7-O₂CCCPh, 8-O₂CCCSiMe₃, 9-O₂CNHPh, and 10-O₂CNHCH₂Ph (KBr)

complex	B-H	C≡C	N-H
7-O ₂ CCCPh	2522, 2551	2211	_
8-O ₂ CCCSiMe ₃	2524, 2558	2184	_
9-O ₂ CNHPh	2522, 2552	_	3279
10-O ₂ CNHCH ₂ Ph	2527, 2550	-	3277



Figure 2. Molecular structure of 7-O₂CCCPh shown with 30% ellipsoids. Selected hydrogen atoms and solvent are omitted for clarity.

downfield of the benzene reference peak and show distinct splitting; the ortho CH group is shifted the most downfield, with the meta and para CH groups located within approximately 0.5 ppm of each other. Analysis by infrared spectroscopy reveals that all carboxylate compounds still show two inequivalent B-H's in the same ranges as those for the starting materials, and no absorptions for carbonyls.

Treating 2-CCPh and 3-CCSiMe₃ with 1 atm of carbon dioxide produces the forest green complexes $Tp_2^*U(\kappa^2-O_2CCCPh)$ (7- O_2CCCPh) and $Tp_2^*U(\kappa^2-O_2CCCSiMe_3)$ (8- $O_2CCCSiMe_3$) in quantitative yields. Most significantly, the infrared spectra have sharp absorption bands at 2211 and 2184 cm⁻¹ assignable to the carbon–carbon triple bonds in 7- O_2CCCPh and 8- $O_2CCCSiMe_3$,

Table 6.	Structural	Parameters	(Distances	in A a	and Ang	les in
deg) for	7-0 ₂ CCC	Ph				

U1-N11 U1-N21	2.656(10) 2.569(10)	U1-O41 U1-O42	2.539(9) 2.512(8)
U1-N31	2.629(11)	O41-C40	1.248(16)
U1-N61 U1-N71	2.568(10) 2.646(11)	O42-C40 C42-C43	1.292(16) 1.197(19)
U1-N81	2.639(10)		
O42-U1-O41 O41-C41-O42	161.2(10) 121.8(11)	C41-C42-C43	178.0(15)

respectively (Table 5). This trend has been observed by Evans, who has recently reported $Cp_2^*U(\kappa^2-O_2CCCPh)_2$, the product from insertion of CO_2 into both U–C bonds in $Cp_2^*U(CCPh)_2$ at 80 psi.⁵ Insertion of carbon dioxide changes the infrared absorption band for the C=C from 2056 cm⁻¹ to 2214 cm⁻¹, similar to the shifts observed for 7-O2CCCPh and 8-O2CC-CSiMe₃. This shifting in the IR absorption band for the carboncarbon triple bond in 7-O2CCCPh is complicated by its conjugation with the π system of both the CO₂ fragment and the phenyl ring, as displayed by the small dihedral angle (15.32 \pm 3.07°) between these two planes. The insertion of CO₂ into the uranium-carbon bonds of 2-CCPh and 3-CCSiMe₃ is reminiscent of that observed by our group for the formation of $Tp_{2}^{*}U(\kappa^{2}-O_{2}CCH_{2}Ph)^{15}$ and by Marks for $Cp_{2}^{*}UMe_{2}$ to form the uranium(IV) diacetate $Cp_2^*U(O_2CCH_3)_2$.⁴ In both cases, CO_2 insertion proceeds readily and quantitatively at low pressures, even at less than 1 atm. The crystal structure of $Cp_2^*U(O_2CCH_3)_2$ was not obtained. However, it was proposed that the acetate ligand adopts either a bidentate or bridging coordination mode.

The solid-state structure of 7-O₂CCCPh was explored by X-ray diffraction of suitable crystals grown from a concentrated THF solution with a trace of toluene at -35 °C (Figure 2 and Table 6). The U–N distances are all as expected and are consistent with those observed for the previously synthesized bis(hydrotris(pyrazolyl)borate) uranium(III) carboxylate complex Tp*₂U(κ^2 -O₂CCH₂Ph).¹⁵ The U–O distances of 2.512(8) and 2.539(9) Å in 7-O₂CCCPh are equivalent within error, as are the C–O distances of 1.248(16) and 1.292(16) Å. The O41–C41–O42 bond angle is 121.8(11)°, supporting *sp*² hybridization of the carboxylate carbon. Comparison of the structural data of 7-O₂CCCPh with those of the previously characterized Tp*₂U(κ^2 -O₂CCH₂Ph) supports the assignment of a uranium(III) center with a monoanionic carboxylate ligand.





The similarity in metrical parameters between the two carboxylate compounds indicates that substitution at the carboxylate carbon has little influence on the overall structure at uranium. Further evidence for the monoanionic character of the carboxylate ligand is obtained by comparison to uranium(VI) carboxylate species, which has similar bond distances and angles.⁴⁸

Although studied for uranium(IV) amide complexes,^{6,7} examples of the insertion of carbon dioxide into U(III)—amide bonds is sparse. Stirring either 4-NHPh or 5-NHCH₂Ph in the presence of small amounts of CO₂ causes an instant conversion to the respective carbamate products $Tp^*_2U(\kappa^2-O_2CNHPh)$ (9-O₂CNHPh) and $Tp^*_2U(\kappa^2-O_2CNHCH_2Ph)$ (10-O₂CNH-CH₂Ph) (eq 2). Confirmation by infrared spectroscopy shows shifts in the N–H peaks to 3279 cm⁻¹ for 9-O₂CNHPh and 3277 cm⁻¹ for 10-O₂CNHCH₂Ph (from 3369 cm⁻¹ for 4-NHPh and 3305 cm⁻¹ for 5-NHCH₂Ph) along with an increase in intensity upon insertion of CO₂. The similarity of the spectroscopic features of these compounds to those of the acetylide derivatives supports a trivalent uranium center with a monoanionic carbamate ligand. Formation of the uranium(III) carbamate by

 $\rm CO_2$ insertion into the U–N bond proceeds in a fashion similar to that for homoleptic uranium(IV) amides.^{10,49}

Likewise, the insertion chemistry of carbon dioxide into the uranium(III)-sulfur bond was probed. Upon addition of 1 atm of CO₂ to a solution of 6-SPh in THF, the dark blue solution turns deep green (eq 3). Stirring followed by removal of the volatiles leaves a dark blue residue. Analysis by ¹H NMR spectroscopy shows that only 6-SPh remains, indicating that insertion of carbon dioxide into the uranium(III)-sulfur bond is reversible. Conducting the reaction of 6-SPh in a J. Young NMR tube allowed for the CO₂-inserted product $Tp_2^*U(\kappa^2-O_2CSPh)$ (11-**O₂CSPh**) to be observed spectroscopically (Figure 3), showing a ¹H NMR spectrum similar to those of the other carboxylate products. The green solution characteristic of the carboxylate derivative persists under 1 atm of CO₂. The para, meta, and ortho phenyl peaks of the sulfide ligand are shifted to 8.50, 8.94, and 13.72 ppm, due to the increased distance from the paramagnetic uranium center. Analogous reactivity has been observed for the tetravalent Cp₃USⁱPr.^{11,50} Insertion of carbon dioxide into the U-S bonds of $Cp_2^*U(S^tBu)_2$ is irreversible, allowing isolation of $Cp_{2}^{*}U(\kappa^{2}-O_{2}CSC(CH_{3})_{3})_{2}$ as a microcrystalline solid.¹¹

The insertion chemistry observed with the family of uranium-(III) complexes presented is in sharp contrast to previous studies with uranium(III). Addition of 1 atm of carbon dioxide to the sterically hindered uranium(III) complex [((^{Ad}ArO)₃tacn)U] produces a charge-separated uranium(IV) species, [((^{Ad}ArO)₃tacn)-U(CO₂)], where a radical is located on the carbon dioxide ligand.⁵¹ Reducing the size of the ortho alkyl substituent to *tert*-butyl does not create an isolable charge-separated species; instead, two uranium centers each reduce carbon dioxide by one electron, creating the μ -oxo dimer [((^{tBu}ArO)₃tacn)U]₂(μ -O). Thus, the trivalent derivatives presented here are unique in that the trivalent uranium center is maintained throughout the reaction and is not oxidized by the CO₂.

As previously demonstrated,¹⁵ carboxylate ligands are effectively released from trivalent uranium centers using trimethylsilyl halides. Addition of trimethylsilyl iodide and trimethylsilyl chloride to $9-O_2CNHPh$ and $10-O_2CNHCH_2Ph$ effectively cleaves the uranium–oxygen bond, generating the uranium monoiodide $Tp^*_2UI^{52} Tp^*_2UCl$,¹⁹ respectively. The same reactivity was observed with $7-O_2CCCPh$ and $8-O_2CCCSiMe_3$; however, the reaction products were impure.

Reactivity with Acetone. To determine if insertion of a more sterically demanding carbonyl substrate is possible, the reactivity of the uranium(III) derivatives with acetone was explored. Acetone is an ideal substrate because it has been previously demonstrated to perform insertion with uranium(IV) organometallics.^{53,54} Treating $Tp^*_2UCH_2Ph$, $Tp^*_2UC\equiv CPh$, and Tp^*_2UNHPh with 1 equiv of dry acetone caused an immediate color change to brown (eq 4). Interestingly, analysis by ¹H NMR spectroscopy shows the same product regardless of the starting material. The typical pattern observed for the phenyl groups that would be expected if insertion happened was noticeably absent. Further, the presence of toluene, phenylacetylene, and aniline was observed, indicating protonation had occurred. Addition of acetone-*d*₆ to the same compounds produces deuterated organics, as evidenced by ²H NMR spectroscopy.



X-ray-quality crystals were obtained from cooling a solution of pentane and toluene (4/1) to -35 °C. Refinement confirmed that insertion had not occurred as anticipated, but rather a new uranium(III) alkoxide species, Tp*2UOC(CH3)CH2 (12-OC- $(CH_3)CH_2$, resulted (Figure 4). The unit cell contains two independent molecules, labeled with U1 and U2 centers (only the molecule containing U1 is presented). The U-N distances for the Tp* ligand for both molecules in the unit cell are within the range of those expected for others with this bis(ligand) framework.^{37,38} The U1-O140 bond is 2.198(9) Å, similar to those observed for other uranium(III) alkoxides (Table 7).²⁹ Analysis of the O140-C141 bond distance of 1.388(19) Å indicates that the carbonyl group has been reduced to a single bond. Furthermore, the distance between C141 and the two adjacent carbons are significantly different, with distances of 1.46(2) and 1.32(2) Å. The shortened C–C bond distances establish that the original methyl group has been deprotonated to form a methylene and is confirmed by the refinement of two hydrogen atoms. Additionally, the central carbon of the alkoxide group forms a planar conformation between the oxygen and two carbons, showing sp^2 -hybridized character has been maintained as a result of the newly formed carbon-carbon double bond.



Figure 4. Molecular structures of **12-OC(CH₃)CH₂** shown with 30% ellipsoids. Selected hydrogen atoms are omitted for clarity.

Table 7.	Structural Parameters	(Distances in A	Å and Angles in
deg) for	$12-OC(CH_3)CH_2$		

U1-N111	2.687(9)	U1-N181	2.679(9)
U1-N121	2.677(9)	U1-O140	2.198(9)
U1-N131	2.548(9)	O140-C141	1.388(19)
U1-N161	2.685(9)	C141-C142	1.46(2)
U1-N171	2.551(9)	C141-C143	1.32(2)
U1-O140-C141	161.2(10)	O140-C141-C143	118.5(17)
O140-C141-C142	119.0(19)	C141-C142-C143	122(2)

Analysis of 12-OC(CH₃)CH₂ by ¹H NMR spectroscopy in benzene- d_6 shows a spectrum typical for uranium(III) derivatives of this ligand set. Two resonances for the methyl peaks on the ligands pointing toward and away from the uranium center are observed at -12.66 and -1.11 ppm, respectively. As expected, the CH on the pyrazole ring appears at 7.09 ppm, while that for the BH appears as a broad singlet at 4.16 ppm. The resonances for the enolate ligand are upfield of the benzene solvent peak, with the methyl group visible at 36.27 ppm and the methylene protons at 34.79 and 35.64 ppm.

The formation of the enolate product is significant, given that metal complexes of this type have been invoked as intermediates in metal-mediated aldol condensations. Upon exposure of **12**-**OC(CH₃)CH₂** to additional amounts of acetone, no further progression to the aldolate occurred. This is in contrast to the case of the related uranium(III) dichloride Tp*UCl₂, which readily forms the aldolate.^{15,54} Insertion of acetone into the U–C bond of Tp*U(Cl₂)CH₂SiMe₃⁵³ has also been observed, forming the aldolate derivative with excess acetone. In contrast to both Tp* uranium examples, addition of acetone to the unsubstituted hydrotris(pyrazolyl)borate uranium(IV) dimethyl compound Tp₂UMe₂ results in insertion of acetone into both methyl groups to form the uranium bis(*tert*-butoxide) Tp₂U(O^tBu)₂.⁵⁴ In comparison, Tp*₂UCH₂Ph is much more sterically hindered than Tp*UCl₂, Tp₂UMe₂, and Tp*U(Cl₂)CH₂SiMe₃, indicating



Scheme 2

$$Tp_{2}^{*}UCH_{2}Ph \xrightarrow{O} \left[Tp_{2}^{*}U \xrightarrow{O} \right] \longrightarrow Tp_{2}^{*}U \xrightarrow{O} \left[Tp_{2}^{*}U \xrightarrow{O} \right] \longrightarrow Tp_{2}^{*}U \xrightarrow{O} \left[Tp_{2}^{*}U \xrightarrow{O} \right]$$

that acetone insertion may not be possible due to its hindered approach to the uranium center.

The formation of aldolate ligands at f-block centers has been studied, with differing mechanisms being proposed for the lanthanides and actinides (Scheme 1). For the former, Teuben has proposed that no carbonyl insertion occurs for $Cp^*{}_2Ln(CH(SiMe_3)_2)$ (Ln = La, Ce).⁵⁵ Instead, protonation of the lanthanide alkyl followed by rearrangement forms an inisolable enolate intermediate, which then reacts by C–C coupling in an aldol fashion to generate the product. For the actinides, Marks also invokes protonation of $Cp^*{}_2Th(Cl)Ru(Cp)(CO)_2$ to generate CpRu(CO)₂H and a new thorium alkyl, but this undergoes insertion of acetone into the Th–C bond to produce the aldolate product.⁵⁶ Thus, insertion is not observed for the lanthanides but is favored for the actinides. Although the oxidation states of these species differ by one electron, these examples both use the bis(Cp*) ligand framework, indicating that their steric environments are similar.

Similar to these pathways, 12-OC(CH₃)CH₂ has resulted from the initial protonation of the alkyl, acetylide, or amide ligand by the acidic hydrogen on the acetone (Scheme 1), in accordance with both mechanisms discussed above (Scheme 2). Unlike the mechanism proposed by Marks,⁵⁶ once the new alkyl is formed, no further insertion of acetone takes place, presumably due to steric crowding from the bulky bis(hydrotris(3,5-dimethylyrazolyl)borate) ligand framework. Instead, like the lanthanide chemistry, rearrangement to the enolate occurs; however, no further C-Ccoupling is noted, as $Tp_2^*UO(CH_2)CH_3$ is the sole product. Thus, the protonation product is presumably the kinetically preferred one, while the enolate is the thermodynamically most stable. This is most likely because formation of the strong uranium-oxygen bond acts as a significant driving force. When the uranium thiolate 6-SPh was stirred with 1 equiv of acetone, no reaction was observed by ¹H NMR spectroscopy. It is possible that a reversible process is occurring for the thiolate complex in analogy to the chemistry of carbon dioxide; however, there is no spectroscopic evidence to support this.

The studies presented herein demonstrate the synthesis of uranium(III) acetylide, amide, and thiolate species via the protonation of a uranium(III) alkyl complex. These complexes readily insert carbon dioxide into their uranium—element bonds to produce the corresponding carboxylate derivatives. Interestingly, these species maintain their trivalent oxidation state, in contrast to previously reported work.^{51,57,58} When the more sterically demanding acetone was utilized, protonation of the uranium—element bond followed by rearrangement resulted in the formation of a new uranium enolate compound. In the presence of excess acetone, no formation of the aldolate product was observed, which is in sharp contrast to previous reports for f-block elements,^{55,56} where aldolate products are commonly observed.

ASSOCIATED CONTENT

Supporting Information. Figures giving ¹H NMR spectra, CIF files giving crystallographic data for the crystal structures determined in this paper, and text giving experimental procedures for X-ray crystallography. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sbart@purdue.edu.

ACKNOWLEDGMENT

We wish to acknowledge Purdue University for funding.

REFERENCES

(1) Zaidlewicz, M.; Pakulski, M. M. Reduction of carbonyl groups: transfer hydrogenation, hydrosilylation, catalytic hydroboration, and reduction with borohydrides, aluminum hydrides, or boranes. In *Science of Syntheses*; De Vries, J. G., Molander, G. A., Evans, P. A., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 2011; Vol. 2, pp 59–131.

(2) Bullock, R. M. In Molybdenum and Tungsten Catalysts for Hydrogenation, Hydrosilylation and Hydrolysis; Wiley-Blackwell: New York, 2010; p 51.

(3) Arai, N.; Ohkuma, T. Reduction of carbonyl groups: hydrogenation. In *Science of Syntheses*; De Vries, J. G., Molander, G. A., Evans, P. A., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 2011; Vol. 2, pp 9-57.

(4) Moloy, K. G.; Marks, T. J. Inorg. Chim. Acta 1985, 110, 127.
 (5) Evans, W. J.; Walensky, J. R.; Ziller, J. W. Organometallics 2010,

(5) Evans, (1. 5), (1. acrisky, 5. 10, 2010) 29, 945.

(6) Arduini, A. L.; Jamerson, J. D.; Takats, J. Inorg. Chem. 1981, 20, 2474.

(7) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. J. Am. Chem. Soc. **2008**, 130, 12536.

(8) Calderazzo, F.; Dell'Amico, G.; Netti, R.; Pasquali, M. Inorg. Chem. 1978, 17, 471.

(9) Calderazzo, F.; Dell'Amico, G.; Pasquali, M.; Perego, G. Inorg. Chem. 1978, 17, 474.

(10) Bagnall, K. W.; Yanir, E. J. Inorg. Nucl. Chem. 1974, 36, 777.

(11) Lescop, C.; Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. J. Organomet. Chem. **1999**, 580, 137.

(12) Dormond, A.; Aaliti, A.; Elbouadili, A.; Moise, C. J. Organomet. Chem. 1987, 329, 187.

(13) Dormond, A.; Elbouadili, A.; Moise, C. J. Organomet. Chem. 1989, 369, 171.

(14) Sharma, M.; Andrea, T.; Brookes, N. J.; Yates, B. F.; Eisen, M. S. J. Am. Chem. Soc. **2011**, 133, 1341.

(15) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. J. Am. Chem. Soc. **2011**, 133, 4948.

(16) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(17) Sheldrick, G. M. Acta Crystallogr. 2008, 112, A64.

(18) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M. *DIRDIF2008 Program System*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 2008.

(19) Antunes, M. A.; Domingos, A.; Cordeiro dos Santos, I.; Marques, N.; Takats, J. *Polyhedron* **2005**, *24*, 3038.

(20) Foyentin, M.; Folcher, G.; Ephritikhine, M. J. Organomet. Chem. 1987, 335, 201.

(21) Evans, W. J.; Walensky, J. R.; Ziller, J. W. Organometallics 2010, 29, 945.

(22) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. Organometallics 2008, 27, 3335.

(23) Newell, B. S.; Rappe, A. K.; Shores, M. P. Inorg. Chem. 2010, 49, 1595.

(24) Stewart, J. L.; Andersen, R. A. Polyhedron 1998, 17, 953.

(25) Mansell, S. M.; Perandones, B. F.; Arnold, P. L. J. Organomet. Chem. 2010, 695, 2814.

(26) Odom, A. L.; Arnold, P. L.; Cummins, C. C. J. Am. Chem. Soc. 1998, 120, 5836.

(27) Nelson, J. E.; Clark, D. L.; Burns, C. J.; Sattelberger, A. P. Inorg. Chem. 1992, 31, 1973.

(28) Nakai, H.; Hu, X.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Inorg. Chem.* **2004**, *43*, 855.

(29) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. J. Am. Chem. Soc. 2011, 133, 9036.

(30) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. J. Am. Chem. Soc. 2004, 126, 14574.

(31) Antunes, M. A.; Ferrence, G. M.; Domingos, A.; McDonald, R.; Burns, C. J.; Takats, J.; Marques, N. *Inorg. Chem.* **2004**, *43*, 6640.

(32) Sun, Y. Ph.D. Thesis, University of Alberta, Calgary, Canada, 1995.
(33) Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, J. W.

Organometallics 2002, 21, 1050.
(34) Arliguie, T.; Lescop, C.; Ventelon, L.; Leverd, P. C.; Thuery, P.;
Nierlich, M.; Ephritikhine, M. Organometallics 2001, 20, 3698.

(35) Roger, M.; Belkhiri, L.; Thuery, P.; Arliguie, T.; Fourmigue, M.; Boucekkine, A.; Ephritikhine, M. Organometallics 2005, 24, 4940.

(36) Roger, M.; Barros, N.; Arliguie, T.; Thuery, P.; Maron, L.; Ephritikhine, M. J. Am. Chem. Soc. **2006**, 128, 8790.

(37) Kraft, S. J.; Walensky, J.; Fanwick, P. E.; Hall, M. B.; Bart, S. C. Inorg. Chem. 2010, 49, 7620.

(38) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. Inorg. Chem. 2010, 49, 1103.

(39) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1999**, 1701.

(40) Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. J. Coord. Chem. 1976, 5, 209.

(41) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. Organometallics 2009, 28, 3350.

(42) Thomson, R. K.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. Eur. J. Inorg. Chem. 2009, 1451.

(43) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, J., D. Organometallics **1990**, *9*, 2124.

(44) Gaunt, A. J.; Scott, B. L.; Neu, M. P. Inorg. Chem. 2006, 45, 7401.

(45) Domingos, A.; Pires de Matos, A.; Santos, I. Polyhedron 1992, 11, 1601.

(46) Evans, W. J.; Miller, K. A.; Hillman, W. R.; Ziller, J. W. J. Organomet. Chem. 2007, 692, 3649.

(47) Evans, W. J.; Miller, K. A.; Ziller, J. W.; DiPasquale, A. G.; Heroux, K. J.; Rheingold, A. L. Organometallics **200**7, *26*, 4287.

(48) Rusanova, J. A.; Rusanov, E. B.; Domasevitch, K. V. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2010, C66, m207.

(49) Jones, R. G.; Karmas, G.; Martin, J., G.A.; Gilman, H. J. Am. Chem. Soc. 1956, 78, 6030.

(50) Leverd, P. C.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. J. Organomet. Chem. **1996**, 507, 229.

(51) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757.

(52) Sun, Y.; McDonald, R.; Takats, J.; Day, V. W.; Eberspacher, T. A. Inorg. Chem. **1994**, 33, 4433.

(53) Domingos, A.; Marques, N.; Pires de Matos, A.; Santos, I.; Silva, M. Organometallics **1994**, *13*, 654.

(54) Campello, M. P. C.; Calhorda, M. J.; Domingos, A.; Galvao, A.; Leal, J. P.; Pires de Matos, A.; Santos, I. *J. Organomet. Chem.* **1997**, 538, 223.

(55) Heeres, H. J.; Maters, M.; Teuben, J. H.; Helgesson, G.; Jagner, S. Organometallics **1992**, *11*, 350.

(56) Sternal, R. S.; Sabat, M.; Marks, T. J. J. Am. Chem. Soc. 1987, 109, 7920.

(57) Castro, L.; Lam, O. P.; Bart, S. C.; Meyer, K.; Maron, L. Organometallics 2010, 29, 5504.

(58) Lam, O. P.; Bart, S. C.; Kameo, H.; Heinemann, F. W.; Meyer, K. Chem. Commun. **2010**, *46*, 3137.