

Synthesis and Characterization of N-Heterocyclic Carbene Complexes of Uranium(III)

Hidetaka Nakai, Xile Hu, Lev N. Zakharov, Arnold L. Rheingold, and Karsten Meyer*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, La Jolla, California 92093-0358

Received October 1, 2003

Reaction of $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}$ (**1**) or $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}$ (**3**) with tetramethylimidazol-2-ylidene (Me_4IMC) yields novel N-heterocyclic carbene complexes $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{Me}_4\text{IMC})$ (**2**) and $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}(\text{Me}_4\text{IMC})$ (**4**). Uranium complexes **2** and **4** represent the first examples of compounds with an N-heterocyclic carbene ligand coordinated to a low-valent uranium center. The paramagnetic complexes **1**, **2**, and **4** were characterized by ^1H NMR, UV–vis–NIR, and EPR spectroscopy as well as SQUID magnetization measurements and X-ray diffraction analyses. DFT studies indicate a significant degree of π -bonding in the U(III)–carbene entity.

N-Heterocyclic carbenes (NHCs) derived from imidazolium salts by deprotonation are well-known ligands in organometallic chemistry. It has been shown that these 1,3-disubstituted imidazol-2-ylidenes coordinate to main group and d-block metals in low and high oxidation states, as well as to lanthanide ions. Numerous metal NHC complexes have been synthesized, characterized, and studied for their potential catalytic application.¹ In contrast, only a few examples of actinide metal complexes employing NHC ligands are reported in the literature. Recently, NHC coordination to a uranyl species has been shown, $[(^{\text{R}}\text{IMC})_2\text{UO}_2(\text{Cl})_2]$ being the only reported example.²

We recently demonstrated that the uranium(III) complex, $[(^{\text{R}}\text{ArO})_3\text{tacn}]\text{U}$ ($\text{R} = \textit{tert}$ -butyl), supported by the aryloxy-functionalized triazacyclononane (tacn) chelator, provides a powerful platform for reactivity studies at the apical position of the electron-rich uranium complex.³

Herein, we report the synthesis and full characterization of N-heterocyclic carbene complexes resulting from reaction of the adamantyl-derivatized tris-aryloxy tacn complex,

$[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}$ ($\text{Ad} = \textit{adamantyl}$, **1**), as well as the archetypal U(III) tris-amido species $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}$ (**3**)⁴ with tetramethylimidazol-2-ylidene (Me_4IMC).

The sterically demanding adamantyl tacn derivative, $(^{\text{Ad}}\text{ArOH})_3\text{tacn}$, was synthesized in high yield (68%) via a Mannich reaction of tacn with 2-adamantyl-4-*tert*-butylphenol.⁵ Treatment of $(^{\text{Ad}}\text{ArOH})_3\text{tacn}$ with 1 equiv of **3** in benzene at rt (room temperature) yields the six-coordinate U(III) complex $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}$ (**1**) as a red-brown powder (67%).⁵ The ^1H NMR spectrum of **1** exhibits the expected 14 paramagnetically shifted and broadened signals between –22 and 14 ppm. Crystals of **1** suitable for X-ray diffraction analysis were grown from a saturated pentane/neopentane solution at rt. The solid-state molecular structure of one of the two independent molecules in crystals of $\mathbf{1}\cdot\text{C}_6\text{H}_{14}$ is depicted in Figure 1.⁶

The coordination polyhedron of the six-coordinate trivalent uranium ion can best be described as distorted trigonal prismatic, with the U(III) center below a trigonal plane of three aryloxy ligands. Weak nitrogen interactions with the tacn polyamine chelator shield one side of the uranium center and prevent unwanted side reactions. Additionally, the open coordination site of the highly reactive U(III) ion is well protected by the adamantyl groups, yet these alkyl substituents are sufficiently flexible to open up and accept ligands and substrates into the reactive cavity. This ligand flexibility is evident from the reaction of **1** with the N-heterocyclic carbene ligand 1,3,4,5-tetramethyl-imidazol-2-ylidene⁷ (Me_4 -

(4) (a) Clark, D. L.; Sattelberger, A. P.; Andersen, R. A. *Inorg. Synth.* **1997**, *31*, 307–315. (b) Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953–958.

(5) See Supporting Information.

(6) Crystallographic details for $\mathbf{1}\cdot\text{C}_6\text{H}_{14}$: $\text{C}_{75}\text{H}_{110}\text{N}_3\text{O}_3\text{U}$, $M = 1339.71$, red-brown block, $T = 100(2)\text{K}$, orthorhombic, space group $P2_12_12_1$, $a = 21.9055(18)\text{Å}$, $b = 23.9529(19)\text{Å}$, $c = 25.759(2)\text{Å}$, $V = 13516.0(19)\text{Å}^3$, $Z = 8$, $R_1 = 0.0720$ [$I > 2\sigma(I)$], $\text{GOF} = 1.274$. Crystallographic details for **2**: $\text{C}_{76}\text{H}_{108}\text{N}_5\text{O}_3\text{U}$, purple block, triclinic, space group $P1$, $a = 11.0692(11)\text{Å}$, $b = 12.1212(12)\text{Å}$, $c = 25.395(3)\text{Å}$, $\alpha = 86.178(2)^\circ$, $\beta = 81.586(2)^\circ$, $\gamma = 84.705(2)^\circ$, $V = 2489(1)\text{Å}^3$, $Z = 2$, $R_1 = 0.0865$ [$I > 2\sigma(I)$], $\text{GOF} = 1.332$. Crystallographic details for **4**: $\text{C}_{25}\text{H}_{66}\text{N}_5\text{Si}_6\text{U}$, dark blue block, $T = 243(2)\text{K}$, monoclinic, space group $P2_1/c$, $a = 11.7530(11)\text{Å}$, $b = 18.2920(17)\text{Å}$, $c = 19.1009(18)\text{Å}$, $\beta = 92.287(2)^\circ$, $V = 4103.2(7)\text{Å}^3$, $Z = 4$, $R_1 = 0.0268$ [$I > 2\sigma(I)$], $\text{GOF} = 1.039$.

(7) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561–562.

* Author to whom correspondence should be addressed. E-mail: kmeyer@ucsd.edu.

(1) (a) Hermann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162–2187. (b) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913–921. (c) Hermann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291–1309.
(2) Oldham, W. J.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Chem. Commun.* **2001**, 1348–1349.
(3) (a) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2002**, 2764–2765. (b) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565–4671.

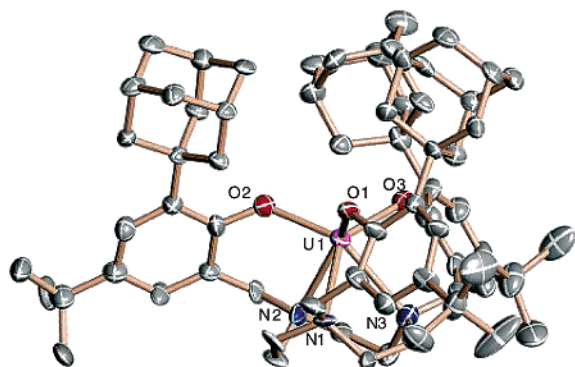
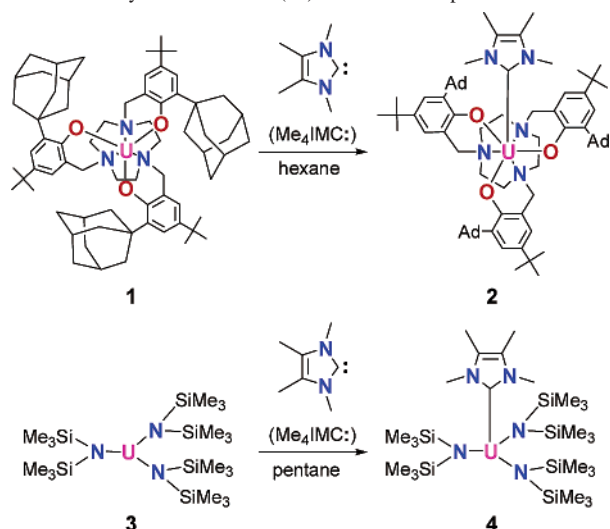


Figure 1. Solid-state molecular structure of $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}$ (**1**) in crystal of $1 \cdot \text{C}_6\text{H}_{14}$. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity, thermal ellipsoids at 50% probability.

IMC:). Treatment of **1** with 1 equiv of $\text{Me}_4\text{IMC:}$ in hexane at rt leads to formation of the deep purple complex $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})$ (**2**) that could be isolated as a crystalline powder in 75% yield.⁸ Similarly, treatment of **3** with $\text{Me}_4\text{IMC:}$ also leads to the formation of a U(III) carbene complex, $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})]$ (**4**, Scheme 1).

Scheme 1. Synthesis of the U(III)–Carbene Complexes



Dark blue crystals of complex **4** were isolated in excellent yield (>90%).⁹ Coordinatively unsaturated **1** and carbene complexes **2** and **4** were characterized by ^1H NMR, X-band EPR, and UV–vis–NIR spectroscopy as well as X-ray diffraction analysis and SQUID magnetization measurements. In the ^1H NMR spectrum, the resonances of the free carbene $\text{Me}_4\text{IMC:}$ in C_6D_6 at δ 1.57 and 3.36 ppm clearly

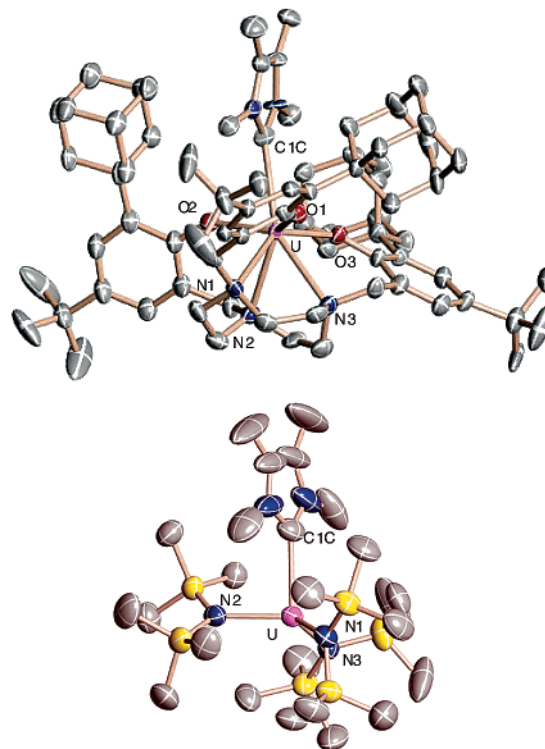


Figure 2. Solid-state molecular structures of $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})$ (**2**) (top) and $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})]$ (**4**) (bottom). Hydrogen atoms are omitted for clarity, thermal ellipsoids at 50% probability.

shift and broaden upon binding to the paramagnetic U(III) center (δ -0.47 and -10.31 ppm in **2**, δ -8.78 and -9.80 ppm in **4**). The UV–vis–NIR spectroscopic data (Figures S1, S2) are also consistent with the coordination of the carbene ligand to a uranium center. The electronic absorption spectrum of six-coordinate **1** displays weak and sharp absorption bands in the visible and near-infrared region between 500 and 2200 nm, characteristic for parity forbidden $f-f$ transitions in trivalent U ions. In addition, an intense charge-transfer (CT) band at 424 nm ($\epsilon = 1945 \text{ M}^{-1} \text{ cm}^{-1}$) is observed. Carbene coordination in **2** causes the CT absorption band to shift to the red (496 nm, $\epsilon = 1533 \text{ M}^{-1} \text{ cm}^{-1}$). Interestingly, this CT band in the spectrum of the corresponding tris-amido system **4** shows a significantly larger bathochromic shift from 478 to 594 nm upon carbene binding. This latter shift indicates a stronger U–carbene interaction in **4** compared to **2**, which is in accord with the shorter U–carbene bond determined by the X-ray diffraction analysis.

The solid-state structures of **2** and **4** were confirmed by X-ray crystallography. The molecular structures of **2** and **4** are depicted in Figure 2. Table 1 summarizes selected structural parameters for **1**, **2**, and **4**.

Although the average U–N(tacn) and U–O(ArO) bond distances in carbene complex **2** are similar to those found in the six-coordinate precursor **1**, the out-of-plane shift, $d(\text{o-o-p})$, in **2** is clearly smaller than that found in **1**. We have shown earlier that the displacement of the uranium ion from an idealized trigonal plane of the aryloxy oxygen atoms exhibits a pronounced dependency on the nature of the axial ligand.³ For instance, this parameter for the corresponding seven-coordinate alkane and acetonitrile species,

(8) $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})$ (**2**): $\text{Me}_4\text{IMC:}$ (25 mg, 0.2 mmol) was added to a solution of **1** (250 mg, 0.2 mmol) in hexane (10 mL) and stirred at room temperature for 4 h. The resulting red-purple solution was filtered, and the volatiles were removed from filtrate under vacuum to give a red-purple solid. Yield: 207 mg (75%). Elemental analysis (%) calcd for **2**: C 66.25, H 7.90, N 5.08. Found: C 66.08, H 7.83, N 5.01.

(9) $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}(\text{Me}_4\text{IMC:})]$ (**4**): $\text{Me}_4\text{IMC:}$ (248 mg, 2.0 mmol) was added to a solution of $[(\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{\text{III}}]$ (1.43 g, 2.0 mmol) in pentane (15 mL) and stirred at room temperature for 1 h. The dark blue solution was stored for 12 h at -35 °C. The resulting dark blue crystals were filtered, washed with cold pentane, and dried in a vacuum. Yield: 1.69 g (91%). Elemental analysis (%) calcd for **4**: C 35.56, H 8.00, N 8.29. Found: C 35.75, H 7.78, N 8.16.

Table 1. Selected Structural Parameters for Complexes **1**, **2**, and **4**^a

	1 ^b	2	4
U–C _{carbene}		2.789(14)	2.672(5)
U–N _{av}	2.64(3)/2.65(2)	2.72(3)	2.362(3)
U–O _{av}	2.22(1)/2.29(1)	2.28(2)	
O–U–O	104.6(3)/103.9(3)	110.4(3)	
	108.1(3)/108.2(3)	111.2(3)	
	107.6(3)/104.8(3)	134.3(3)	
N–U–N	67.6(3)/67.2(3)	65.7(3)	115.07(11)
	67.1(3)/67.6(3)	64.6(3)	
	66.2(4)/67.5(3)	64.1(3)	
U _{out-of-plane} shift	−0.834/−0.873	−0.263	+0.532

^a Bond distances in Å, bond angles in deg. ^b Values for two independent molecules.

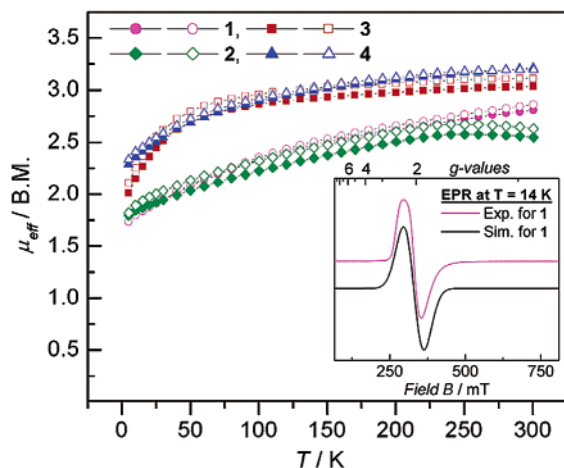


Figure 3. SQUID magnetization measurement of **1**, **2**, **3**, and **4** (5–300 K, in duplicate) and X-band EPR spectrum of **1** (inset) recorded in frozen benzene solution. Experimental conditions: microwave frequency, 9.4666 GHz; power, 0.63 mW; modulation amplitude, 10 G. Simulated parameters: $g = 2.005$. Line widths: $W_{\text{fwhm}} = 400$ G.

$[(^t\text{BuArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{alkane})$ and $[(^t\text{BuArO})_3\text{tacn}]\text{U}^{\text{III}}(\text{NCCH}_3)$, were determined to be -0.44 and -0.66 Å, respectively. The U(III) displacement in six-coordinate **1** with no axial ligand was calculated to be -0.85 Å below the $(\text{ArO})_3$ plane. Upon carbene coordination, however, the U ion moves toward the plane and is found at -0.26 Å, indicative of a significant orbital interaction between the carbene center and the uranium ion. The U(III)–C(carbene) bond distances in **2** and **4** were determined to be 2.789(14) and 2.672(5) Å. The slightly shorter U(III)–carbene bond distance found in tris-amido system **4** is consistent with the UV–vis–NIR spectroscopic features of the complexes (vide supra).

Paramagnetic compounds **1–4** were characterized by low-temperature X-band EPR spectroscopy and variable temperature SQUID magnetization measurements (Figures 3, S3, S4). The magnetic moment, μ_{eff} , of solid samples of **1–4** is temperature dependent, varying from 1.74, 1.81, 2.06, and 2.31 μ_{B} at 5 K to 2.83, 2.59, 3.07 and 3.20 μ_{B} at 300 K.

The experimentally determined effective magnetic moment at room temperature is considerably lower than that calculated for the free-ion moment of a trivalent uranium ion with an f^3 electron configuration ($\mu_{\text{eff}}(\text{calcd}) = 3.69 \mu_{\text{B}}$).¹⁰

(10) $\mu_{\text{eff}}(\text{calcd}) = g_J J(J+1)^{1/2}$, with the intermediate-coupling Landé splitting factor for U^{3+} $g_J = 0.743$, for $^4I_{9/2}$, J is $9/2$. Jones E. R.; Hendricks, M. E.; Stone, J. A.; Karraker, D. G. *J. Chem. Phys.* **1974**, *60*, 2088.

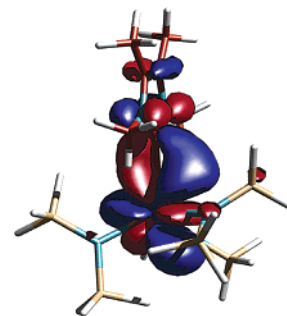


Figure 4. Singly occupied molecular orbital depicted for the second most energetic electron in the system of **4** (SOMO–2).

However, the magnetic behavior of **3**, in the temperature range between 50 and 300 K, as well as the room-temperature moments of **1**, **2**, and **4**, compare well with that reported by Andersen et al.^{4b} and others.¹¹ The X-band EPR spectrum of **1**, recorded in frozen benzene solution at 14 K, exhibits an isotropic signal at $g = 2.005$ (Figure 3), which is identical to the one recorded for $[(^t\text{BuArO})_3\text{tacn}]\text{U}^{\text{III}}$ and similar to the one that we measured for the parent tris-amido system **3** ($g = 2.50$, Figure S4). EPR and SQUID data of molecular uranium complexes for comparison are exceedingly rare. A detailed and systematic analysis is currently underway and will be presented in a full article.

The nature of the U(III)–carbene interaction was further examined by computational analysis (BP86/TZP, ZORA, ADF 2003.01). Figure S5 displays the molecular orbitals for the three most energetic electrons in the system of **4**. Interestingly, visual inspection of SOMO–2 (Figure 4) indicates that the carbene coordinates to the electron-rich U(III) ion through π -bonding interaction, involving f -type uranium orbitals and π -type orbitals of the carbene ligand.

In conclusion, novel N-heterocyclic carbene complexes of U(III) were successfully synthesized and fully characterized. The experimental as well as computational results indicate that the N-heterocyclic carbene coordinates to the electron-rich U(III) ion through π -bonding interaction. From these findings we conclude that the carbon center of an NHC is capable of acting as a π -accepting ligand and thereby supports the stabilization the electron-rich U ion.

Acknowledgment. This work was supported by UCSD and the ACS-PRF Type G grant. We thank Dr. Peter Gantzel and Ms. Ingrid Castro-Rodriguez for help with the crystallography. We thank Prof. Daniel Mindiola for a generous gift of $(\text{THF})_4\text{UI}_3$ starting material.

Supporting Information Available: Experimental details for the free ligand $(^{\text{Ad}}\text{ArOH})_3\text{tacn}$, **1**, **2**, and **4**, crystallographic data of $(^{\text{Ad}}\text{ArOH})_3\text{tacn}$, **1**, **2**, and **4** in CIF format, UV–vis–NIR spectra, ^1H NMR spectra, and SQUID data for **1**, **2**, **3**, and **4**, EPR spectra of **1**, **2**, **3**, and **4**, and computational details for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC035142J

(11) (a) $[(\text{N}_3\text{N})\text{U}] \mu_{\text{eff}}(293 \text{ K}) = 3.06 \mu_{\text{B}}$: Roussel P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070–1071. (b) $[(\text{Me}_3\text{Si})_2\text{CH}_3\text{U}] \mu_{\text{eff}}(300 \text{ K}) = 3.00 \mu_{\text{B}}$: Van der Sluys, W. G.; Burns, C. J.; Sattelberger A. P. *Organometallics* **1989**, *8*, 855–857. (c) $[(\text{Ar}(\text{R})\text{N})_3\text{U}(\text{THF})] \mu_{\text{eff}}(291 \text{ K}) = 2.95 \mu_{\text{B}}$: Odom, A. L.; Arnold, P. L.; Cummins C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836–5837.