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-ylidene 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. 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, [(Me₄IMC):UO₂Cl₂] being the only reported example.

We recently demonstrated that the uranium(III) complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl), supported by the aryl-oxide-functionalized triazacyclononane (tacn) chelator, provides a powerful platform for reactivity studies at the apical position of the electron-rich uranium complex. Herein, we report the synthesis and full characterization of N-heterocyclic carbene complexes resulting from reaction of the adamantly-derived tris-aryloxide tacn complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl, 1), as well as the archetypal U(III) tris-amido species [(Me₃Si)₂N]₃U(III) (3) with tetramethylimidazol-2-ylidene (Me₄IMC:).

The sterically demanding adamantly tacn derivative, (AdOH)tacn, was synthesized in high yield (68%) via a Mannich reaction of tacn with 2-adamantyl-4-tert-butyl-phenol. Treatment of (AdOH)tacn with 1 equiv of benzene at rt (room temperature) yields the six-coordinate U(III) complex [(AdArO)₃tacn]U(III) (1) as a red-brown powder (67%). 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 1-C₆H₁₄ is depicted in Figure 1.

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 arylxide 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 adamantly 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-ylidene (Me₄IMC:).

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-ylidene 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. 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, [(Me₄IMC):UO₂Cl₂] being the only reported example.

We recently demonstrated that the uranium(III) complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl), supported by the aryl-oxide-functionalized triazacyclononane (tacn) chelator, provides a powerful platform for reactivity studies at the apical position of the electron-rich uranium complex.

Herein, we report the synthesis and full characterization of N-heterocyclic carbene complexes resulting from reaction of the adamantly-derived tris-aryloxide tacn complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl, 1), as well as the archetypal U(III) tris-amido species [(Me₃Si)₂N]₃U(III) (3) with tetramethylimidazol-2-ylidene (Me₄IMC:).

The sterically demanding adamantly tacn derivative, (AdOH)tacn, was synthesized in high yield (68%) via a Mannich reaction of tacn with 2-adamantyl-4-tert-butyl-phenol. Treatment of (AdOH)tacn with 1 equiv of benzene at rt (room temperature) yields the six-coordinate U(III) complex [(AdArO)₃tacn]U(III) (1) as a red-brown powder (67%). 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 1-C₆H₁₄ is depicted in Figure 1.

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 arylxide 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 adamantly 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-ylidene (Me₄IMC:).

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-ylidene 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. 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, [(Me₄IMC):UO₂Cl₂] being the only reported example.

We recently demonstrated that the uranium(III) complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl), supported by the aryl-oxide-functionalized triazacyclononane (tacn) chelator, provides a powerful platform for reactivity studies at the apical position of the electron-rich uranium complex.

Herein, we report the synthesis and full characterization of N-heterocyclic carbene complexes resulting from reaction of the adamantly-derived tris-aryloxide tacn complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl, 1), as well as the archetypal U(III) tris-amido species [(Me₃Si)₂N]₃U(III) (3) with tetramethylimidazol-2-ylidene (Me₄IMC:).

The sterically demanding adamantly tacn derivative, (AdOH)tacn, was synthesized in high yield (68%) via a Mannich reaction of tacn with 2-adamantyl-4-tert-butyl-phenol. Treatment of (AdOH)tacn with 1 equiv of benzene at rt (room temperature) yields the six-coordinate U(III) complex [(AdArO)₃tacn]U(III) (1) as a red-brown powder (67%). 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 1-C₆H₁₄ is depicted in Figure 1.

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 arylxide 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 adamantly 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-ylidene (Me₄IMC:).

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-ylidene 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. 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, [(Me₄IMC):UO₂Cl₂] being the only reported example.

We recently demonstrated that the uranium(III) complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl), supported by the aryl-oxide-functionalized triazacyclononane (tacn) chelator, provides a powerful platform for reactivity studies at the apical position of the electron-rich uranium complex.

Herein, we report the synthesis and full characterization of N-heterocyclic carbene complexes resulting from reaction of the adamantly-derived tris-aryloxide tacn complex, [(AdArO)₃tacn]U(III) (Ad = adamantyl, 1), as well as the archetypal U(III) tris-amido species [(Me₃Si)₂N]₃U(III) (3) with tetramethylimidazol-2-ylidene (Me₄IMC:).

The sterically demanding adamantly tacn derivative, (AdOH)tacn, was synthesized in high yield (68%) via a Mannich reaction of tacn with 2-adamantyl-4-tert-butyl-phenol. Treatment of (AdOH)tacn with 1 equiv of benzene at rt (room temperature) yields the six-coordinate U(III) complex [(AdArO)₃tacn]U(III) (1) as a red-brown powder (67%). 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 1-C₆H₁₄ is depicted in Figure 1.
Treatment of 1 with 1 equiv of Me₄IMC: in hexane at rt leads to formation of the deep purple complex \([((\text{Ad ArO})_3\text{tacn})\text{U}^{III}(\text{Me}_4\text{IMC:})] (2)\) that could be isolated as a crystalline powder in 75% yield. Similarly, treatment of 3 with Me₄IMC: also leads to the formation of a U(III) carbene complex, \([((\text{Me}_3\text{Si})_2\text{N})_3\text{U}^{III}(\text{Me}_4\text{IMC:})] (4, \text{Scheme } 1)\).

Dark blue crystals of complex 4 were isolated in excellent yield (>90%). 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 Me₄IMC: in C₆D₆ at \(\delta = 1.57\) and 3.36 ppm clearly shift and broaden upon binding to the paramagnetic U(III) center (\(\delta = -0.47\) and \(-10.31\) ppm in 2, \(\delta = -8.78\) and \(-9.80\) 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(aryl) 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 aryloxide oxygen atoms exhibits a pronounced dependency on the nature of the axial ligand. For instance, this parameter for the corresponding seven-coordinate alkane and acetonitrile species,
Table 1. Selected Structural Parameters for Complexes 1, 2, and 4

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>U–C_carbene</td>
<td>2.789(14)</td>
<td>2.677(5)</td>
<td></td>
</tr>
<tr>
<td>U–N_av</td>
<td>2.64(3)/2.68(2)</td>
<td>2.72(3)</td>
<td>2.362(3)</td>
</tr>
<tr>
<td>U–O_v</td>
<td>2.22(1)/2.29(1)</td>
<td>2.28(2)</td>
<td></td>
</tr>
<tr>
<td>O–U–O</td>
<td>104.6(3)/103.9(3)</td>
<td>110.4(3)</td>
<td></td>
</tr>
<tr>
<td>N–U–N</td>
<td>67.6(3)/67.2(3)</td>
<td>65.7(3)</td>
<td>115.07(11)</td>
</tr>
<tr>
<td>U_out-of-plane shift</td>
<td>−0.834/−0.873</td>
<td>−0.263</td>
<td>+0.532</td>
</tr>
</tbody>
</table>

* Bond distances in Å, bond angles in deg. * 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: $W_{vis}$ = 400 G.

[(t-BuArO)$_3$tacn]U$^{III}$ (alkane) and [(t-BuArO)$_3$tacn]U$^{III}$ (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 (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 $t^6$ electron configuration (μ$_{eff}$(calcld) = 3.69 μ$_B$).$^{10}$

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.$^{1b}$ 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-BuArO)$_3$tacn]U$^{III}$ 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 (THF)$_4$UI$_3$ starting material.

Supporting Information Available: Experimental details for the free ligand ((t$^{19}$ArOH)$_3$tacn), 1, 2, and 4, crystallographic data of ((t$^{19}$ArOH)$_3$tacn), 1, 2, and 4 in CIF format, UV–vis–NIR spectra, $^1$H 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) [N3N]U μ$_{eff}$(293 K) = 3.06 μ$_B$; Roussel P.; Scott, P. J. Am. Chem. Soc. 1998, 120, 1070–1071. (b) [(Me$_2$Si)$_2$(CH)$_2$]U μ$_{eff}$(300 K) = 3.00 μ$_B$; Van der Sluis, W. G.; Burns, C. J.; Sattelberger A. P. Organometallics 1989, 8, 855–857. (c) [Ar(R)N]$_3$U(THF) μ$_{eff}$(291 K) = 2.95 μ$_B$; Odom, A. L.; Arnold, P. L.; Cummins C. J. Am. Chem. Soc. 1998, 120, 5836–5837.