

Evidence for Alkane Coordination to an Electron-Rich Uranium Center

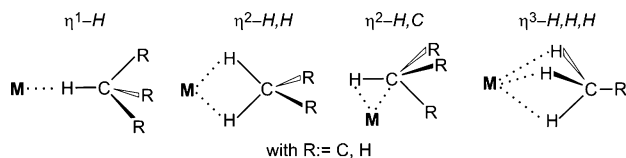
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Metal–alkane complexes are believed to be key intermediates in C–H activation processes. The C–H σ bond of saturated hydrocarbons is strong and notoriously unreactive, and thus, selective intermolecular carbon–hydrogen bond activation has been identified as a fundamental and practical challenge to synthetic chemists.¹ Although theoretical chemists have made significant progress to elucidate the fundamental nature of metal–alkane interactions, detailed structural information for metal–alkane adducts is exceedingly rare. Most known examples of transition metal–alkane complexes to date have been detected in gas phases, matrices, and solutions in situ.² In virtually all reported cases, the metal–alkane adducts were identified spectroscopically as fleeting intermediates at cryogenic temperatures.

Noteworthy exceptions were recently reported by George et al.³ and Gefதாக and Ball.⁴ The latter group generated a cyclopentane adduct, $[(\text{Cp})\text{Re}(\text{CO})_2(\text{C}_5\text{H}_{10})]$, via photolysis of $[(\text{Cp})\text{Re}(\text{CO})_3]$ that was detected NMR-spectroscopically as an intermediate in neat cyclopentane solution at -93°C . On the basis of a comparison of the experimentally determined ^{13}C and ^1H coupling constants and chemical shifts with those of structurally closely related, β -agostic bonded C–H moieties, an $\eta^2\text{-H,C}$ metal–alkane interaction was proposed (see below).

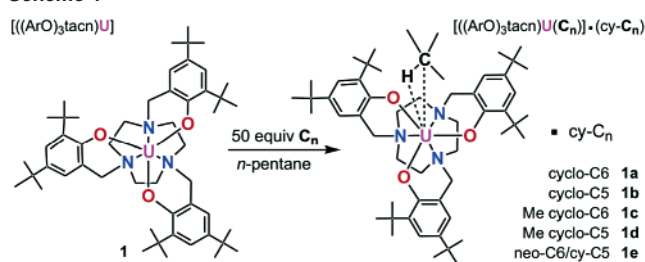


In 1997, Reed et al. reported the only example of an X-ray diffraction analysis of a simple alkane in the coordination sphere of a metal complex.⁵ In this iron porphyrin complex, $(\text{dap})\text{Fe}(\textit{n}\text{-heptane})$, the hydrophobic pocket of a double A-framed porphyrin supported the heptane–iron adduct through a host/guest effect.

We report here the X-ray diffraction analysis of a series of alkane adducts of the low-valent, coordinatively unsaturated, tris-aryl oxide uranium(III) complex $[(\text{ArO})_3\text{tacn}]\text{U}$ (**1**, Scheme 1).^{6,7} These species exhibit evidence for bonding interactions between the uranium ion as well as the macrocyclic ligand and the axial alkane and, thus, raise the question whether the axial alkane is held in place through metal–alkane coordination, a host–guest effect, or a combination of both.

Recrystallization of highly reactive **1** from neat *n*-pentane, *n*-hexane, benzene, and/or toluene, or mixtures thereof, did not yield single crystals suitable for X-ray diffraction analysis. We found, however, that cube-shaped, red-brown crystals could be obtained from an *n*-pentane solution if trace amounts of cyclohexane were present in the glovebox atmosphere. If a solution of **1** in *n*-pentane is treated with 50 equiv of cyclohexane or cyclopentane, cube-shaped crystals of $[(\text{ArO})_3\text{tacn}]\text{U}(\text{cy-C6})\cdot(\text{cy-C6})$ (**1a**) and $[(\text{ArO})_3\text{tacn}]\text{U}(\text{cy-C5})\cdot(\text{cy-C5})$ (**1b**) can be isolated reproducibly.

Scheme 1

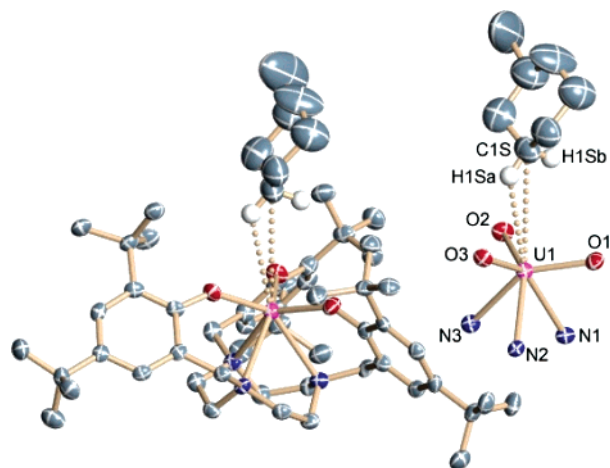


The X-ray diffraction analysis of both complexes clearly revealed atom positions and connectivities of one molecule of cycloalkane in the coordination sphere of the uranium(III) center and a second molecule of cycloalkane cocrystallized in the lattice. The quality of the X-ray data, however, did not allow for discussion of metric parameters. As a result, the solid-state structure of **1a** and **1b** could only be refined isotropically with the cycloalkane modeled as a rigid body.⁸ In contrast, single crystals obtained from *n*-pentane solutions with methyl cyclohexane (**1c**), methyl cyclopentane (**1d**), and neohexane (**1e**) produced good diffraction data. Molecules **1a–e** are isostructural and isomorphous and crystallize in the monoclinic space group $P2_1/n$. All complexes contain an additional solvent molecule in the crystal lattice that is distant from the uranium atom and often disordered. The X-ray analysis of **1c** and **1e** resulted in high-angle diffraction data, revealing rotationally twinned structures along the *a* axis. Crystals of $[(\text{ArO})_3\text{tacn}]\text{U}(\textit{neo}\text{-C6})\cdot(\text{cy-C5})$ (**1e**) were obtained from a competition experiment, in which an *n*-pentane solution of **1** was treated with cyclopentane and neohexane (1:1). Interestingly, the solid-state structure revealed that the two solvent molecules show a high site preference.⁸ While the neohexane molecule predominantly occupies the apical position of the uranium center, the cyclopentane molecule cocrystallizes in the lattice. Compared to all other carbon atoms of the apical solvent molecules in **1c**, **1d**, and **1e**, carbon C1S in closest proximity to the uranium ion exhibits significantly smaller thermal ellipsoids.⁸ This likely can be attributed to decreased thermal activity resulting from coordination to the uranium ion. Thus, crystallographic data for **1c–e** (Table 1) allow for a more detailed discussion of the complexes' core and especially the U–C1S metric parameters. Figure 1 shows the molecular structure of **1c** representative of the series of uranium–alkane complexes reported herein. The structure of the $(\text{ArO})_3\text{tacn}]\text{U}$ core fragment of all alkane adducts is similar to that found for the previously reported seven-coordinate complex $[(\text{ArO})_3\text{tacn}]\text{U}(\text{NCCH}_3)$ (**2**).⁹ The average U–N(tacn) and U–O(ArO) bond distances in **1c**, for instance, were determined to be 2.676(4) and 2.244(3) Å, which are comparable to 2.699(6) and 2.265(5) Å found in **2**.

A significant difference between the solid-state molecular structures of **1c–e** and **2** is the out-of-plane shift, $d(\text{Uo-o-p})$, of the uranium center from an idealized trigonal plane formed by the

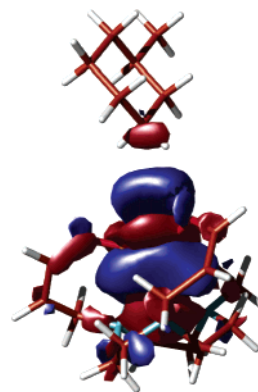
Table 1. Selected Crystal Data, Bond Lengths (Å), and Angles (°) for Uranium Alkane Complexes $[(\text{ArO})_3\text{tacn}]\text{U}(\text{C}_n)]\cdot(\text{cy-C}_n)$

	1c	1d	1e
crystal system		monoclinic	
space group		$P2_1/n$	
unit cell	$a = 19.879(7)$	$a = 19.575(7)$	$A = 19.426(3)$
dimensions	$b = 15.325(5)$	$b = 15.215(6)$	$b = 15.115(2)$
(Å/°)	$c = 20.458(7)$	$c = 20.418(8)$	$c = 20.453(3)$
	$\beta = 92.102(10)$	$\beta = 90.666(6)$	$\beta = 90.117(2)$
Volume (Å ³)	6228(4)	6081(4)	6004.7(13)
R-value (%)	4.82	6.70	5.51
$\angle(\text{O-U-O})$	111.9(1)	112.2(3)	111.6(2)
$d(\text{U-N})_{\text{av}}$	2.676(4)	2.683(9)	2.676(8)
$d(\text{U-O})_{\text{av}}$	2.244(3)	2.261(8)	2.233(5)
$d(\text{U-C1S})$	3.864(7)	3.798(9)	3.731(8)
$d(\text{U-H1Sa})$	3.192	3.228	3.358
$d(\text{U-H1Sb})$	3.591	3.477	3.606
$d(\text{U-H1Sc})$			3.629
$d(\text{Uo-o-p})$ shift	-0.66	-0.64	-0.66

**Figure 1.** Solid-state molecular structure of $[(\text{ArO})_3\text{tacn}]\text{U}(\text{Me}_{\text{cy-C6}})$ (**1c**), with dotted lines emphasizing the $\eta^2\text{-H,C}$ mode. Hydrogen atoms and cocrystallized solvent molecule are omitted for clarity; thermal ellipsoids at 50% probability.

three aryloxy oxygen atoms toward the polyamine chelator. The uranium displacements in **1c–e** were determined to be 0.66 Å below the aryloxy plane. In contrast, $d(\text{Uo-o-p})$ in **2** was determined to be 0.44 Å, which is indicative of a pronounced covalent $\text{U(III)}\text{-NCCH}_3$ interaction.⁹

The uranium–carbon bond distances, $d(\text{U-C1S})$, in **1c** and **1d** were determined to be 3.864 and 3.798 Å, with the shortest U–C bond distance of 3.731 Å found in the solid-state structure of complex **1e**. Additionally, structures **1a–e** exhibit short contacts between the peripheral *tert*-butyl groups and the axial alkane ligand.⁸ These contacts are observed in a range between 2.12 and 2.71 Å and may additionally support the observed alkane coordination. X-ray diffraction analysis of complexes **1c–e** allows for calculation of the hydrogen atoms in proximity to the uranium center (calcd positions, $d(\text{C-H}) = 0.96$ Å). For all structures, an $\eta^2\text{-H,C}$ orientation is observed that seems to be favored for the metal–alkane binding mode. The sum of the van der Waals radii for a U–CH₂ or U–CH₃ contact was determined to be 3.9 Å;^{10–12} thus, we consider the shorter U–C distances reported here indicative of a significant orbital interaction.

**Figure 2.** Singly occupied molecular orbital depicted for the second most energetic electron in the system of **1c** (SOMO-2).

The nature of this interaction was further examined with the aid of a computational analysis. Preliminary DFT studies (BP86/TZP, ZORA, ADF 2003.01) on the core structure indicate a σ -type orbital interaction, mainly composed of the $\text{U}(fz^3)$ orbital and minor contributions (<2%) from C/H(s/p)-type orbitals (Figure 2).⁸

The computed geometry-optimized structure reproduces the experimentally determined core structure very well.⁸ Even without the potentially stabilizing *tert*-butyl groups, which were excluded from this computation, the results support a weak metal–alkane orbital interaction ($E_{\text{BDA}} = 11$ kJ/mol) as well as the observed $\eta^2\text{-H,C}$ coordination mode. The slightly larger calculated U–C and U–H distances⁸ can be attributed to the missing ligand–alkane interactions as observed in the crystal structure that may further stabilize the observed complex.

Acknowledgment. This work was supported by UCSD and the ACS-PRF Type G grant. We thank Prof. Cummins (MIT) for insightful discussions. Xile Hu (UCSD) is acknowledged for help with the computational study.

Supporting Information Available: Experimental, analytical, and computational details, ORTEP plots of **1a–1e**, and details of the refinements (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0379316