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C−H Bond Activation with Actinides: The First Example of Intramolecular Ring Bite of a Pentamethylcyclopentadienyl Methyl Group

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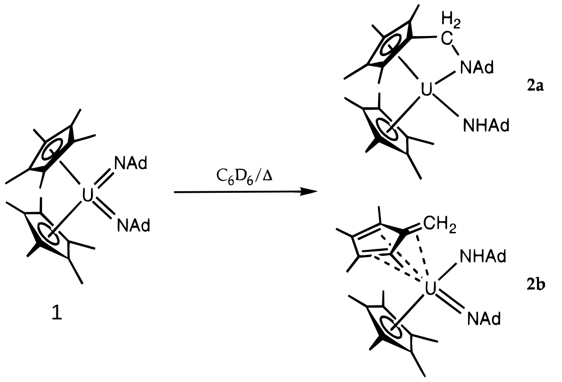
*Summary: Thermolysis of $(C_5Me_5)_2U({=}NAd)_2$, **1** (Ad = 1-adamantyl), in benzene or hexane results in the intramolecular C−H bond activation of a methyl group on a pentamethylcyclopentadienyl ligand across the two imido functional groups. The product of this reaction has been spectroscopically and structurally characterized. The activation product is a reduced U(IV) metallocene bis(amide) complex with an N-bound methylene unit derived from the methyl group attached to one amide group. The activation parameters for this process have been determined; the results are consistent with a simple unimolecular process. This is the first example of intramolecular activation of a (C_5Me_5) methyl C−H bond in an actinide complex.*

We have long been interested in the synthesis and reactivity of high-valent actinide complexes. Much of our research thus far has involved the investigation of ligand sets that support uranium−ligand multiple bonds, which stabilize high-valent species. In particular, we have investigated the structure and reactivity of uranium(VI) bis(imido) and imido−oxo complexes.[1−4] These complexes display a dearth of reactivity; despite the formal electron count of the uranium center being greater than 18, the nitrogen atoms in the imido ligands are not markedly nucleophilic and do not undergo cycloaddition reactions with unsaturated organic molecules, as has been observed for imido complexes of the early transition metals.[5]

The only reactions that we have previously observed with the U(VI) imido compounds are reductions by H_2[1] and silanes,[6] to form the corresponding U(IV) bis(amide) complexes, and catalytic disproportionation of 1,2-diphenylhydrazine to form aniline and azobenzene.[1] Hydrogenation studies showed greater reactivity for alkyl-substituted imido complexes than for analogous arylimidos, suggesting that alkylimido ligands are more nucleophilic than their arylimido analogues. Therefore, thermolysis of an alkylimido complex in C_6H_6 was undertaken to determine if activation of arene C−H bonds would be observed, as in group 4 metal−imido complexes.[5] We herein report that $(C_5Me_5)_2U({=}NAd)_2$, **1** (Ad=1-adamantyl), undergoes a thermal activation of the C_5Me_5 methyl C−H bond, to result in a methylene-tethered bidentate cyclopentadienyl/amide ligand similar to constrained geometry ligand sets reported by Bercaw and Stevens.[7] While activation of the methyl groups on C_5Me_5 is not unprecedented,[8−14] this is the first example of intramolecular C−H activation involving the methyl groups of C_5Me_5 in an actinide complex.[15]

When the symmetrical, diamagnetic compound **1** is heated in solution, a new product is formed (eq 1). The transformation of **1** to the product was monitored by ^1H NMR.[16] The NMR spectrum of **1** displays a single resonance identified as the methyl group protons on the C_5Me_5 ligand and the resonances arising from the two symmetry equivalent adamantyl groups. Upon ther-



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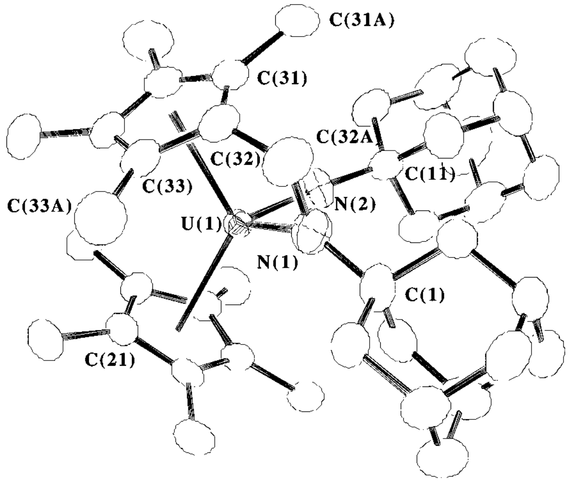

Figure 1. Thermal ellipsoid plot of **2a**. All hydrogen atoms have been omitted for clarity. Bond distances and angles for **2a** are included in the Supporting Information.

molysis, the local symmetry is disrupted, and the product shows one distinct C_5Me_5 resonance, four additional unique methyl groups, two sets of adamantyl resonances, and two diastereotopic methylene protons. The NMR of the product was also paramagnetically shifted, which indicated the product was a reduced U(IV) species and further complicated identification efforts. However, the ^1H NMR data were consistent with two possible structures, **2a** and **2b**, shown in eq 1.

To distinguish between the two proposed structures for **2**, an X-ray crystal structure determination was undertaken.[17] The activation product was found to be a U(IV) metallocene with an N-bound methylene derived from a C_5Me_5 methyl group and a second adamantyl amide functionality (Figure 1).

The constrained geometry of the bifunctional amide–cyclopentadienide ligand gives rise to distortions in the metallocene geometry. The N-bound methylene derived from a C_5Me_5 methyl group is pulled out of the plane of the C_5 ring toward the metal center (displacement from the mean plane is 0.52 Å, in comparison with a mean displacement of the other four methyl groups of 0.16 Å away from the uranium center). This distortion also affects the ring carbon metal distances. The U(1)–C(32) bond is relatively short (2.653(2) Å), the distances U(1)–C(31) and U(1)–C(33) are of intermediate length (2.713(6) and 2.725(7) Å, respectively), and the remaining two uranium–ring carbon bonds are longest (U(1)–C(34) = 2.858(6) Å and U(1)–C(35) = 2.808(6) Å). This reflects a tilting of the C_5 ring; there is no evidence of ring puckering. Not surprisingly, the U–C_5Me_5 (centroid) distance of the activated C_5Me_5 ligand is shorter (2.48 vs 2.55 Å) than the unactivated C_5Me_5 group. The U–N bond distances differ by about 0.08 Å, with the methylene-bound U–N distance being elongated. These U–N bond distances of 2.231(6) Å for U–N(1) and 2.155(7) Å for U–N(2) are consistent with other uranium(IV) amide complexes[18–20] and are significantly longer (0.20 Å) than reported U–N imido bonds.[2,4] Bond angle data are also consistent with the formation of a U(IV) complex. While the U–N–C bond angle for bis(imido) complexes is nearly linear,[2,4] the same U–N–C angles in **2a** are 135.3(5)° for U–N(1)–C(1) and 161.0(6)° for U–N(2)–C(11). These bond angles are consistent with other uranium bis(amide) complexes.[18–21]

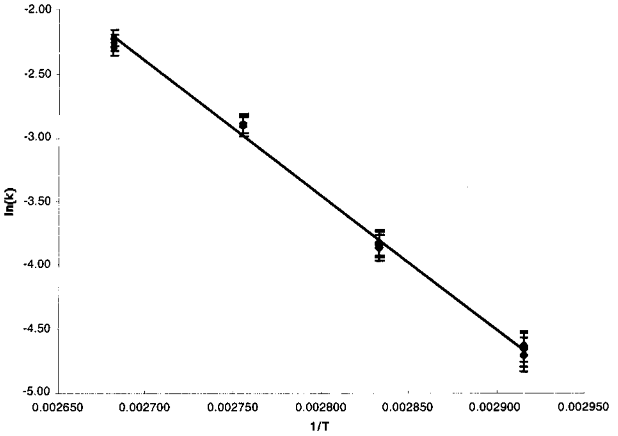

Figure 2. Arrhenius plot of transformation from **1** to **2a**.

The conversion of **1** to **2a** proceeded cleanly in C_6D_6, permitting investigation of the kinetics of activation. Figure 2 shows an Arrhenius plot of the conversion of **1** to **2a**. Not surprisingly, this reaction was first-order with respect to uranium concentration. Thermodynamic data obtained from the Arrhenius plot shows the $\Delta H^{\ddagger}$ of 21 ± 1 kcal/mol, $\Delta S^{\ddagger} = 2.00 \pm 0.09$ eu, which yields a $\Delta G^{\ddagger}$ of 21 ± 1 kcal/mol at 70 °C.

Another system that displays this kind of C–H bond activation was recently reported.[13] The tantalum imido complex $(C_5Me_5)_2Ta({=}NCMe_3)H$, when treated with $[Ph_3C]^+[B(C_6F_5)_4]^-$, undergoes activation of a methyl group on a C_5Me_5 ligand to produce a similar N-bound methylene activation product. The explanation suggested for the observed product formation versus a metal-bound activation product was the extra stability derived from a pseudo-five-membered ring as compared to the more strained pseudo-four-membered ring of a metal-bound species. This thermodynamic product is the only observed product during activation; only **1**and **2a** are observable in solution during thermolysis, but the mechanistic implications are unclear, as intermediates such as a metal-bound methylene $[C_5Me_4CH_2{-}M]$ may go undetected in solution.[13]

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(16) Synthesis of **2a.** A Schlenk tube was charged with $(C_5Me_5)_2U(NAd)_2$ (0.403 g, 0.50 mmol) and benzene (10 mL). The tube was sealed and heated at 80 °C for 5 h, after which time the reaction was judged complete by ^1H NMR. The benzene was removed under vacuum, and the residue was extracted with pentane to leave **2a** (0.320 g, 0.40 mmol, 80% yield). Anal. Calcd for $C_{40}H_{60}N_2U$: C, 59.53; H 7.49; N, 3.47. Found: C, 59.78; H, 7.66; N, 3.45. ^1H NMR (250 MHz, C_6D_6): δ −30.81 (s, 3H), −26.69 (s, 3H), −22.24 (s, 3H), −6.74 (d, J = 11 Hz, 3 H), −5.41 (s, 3H), −4.64 (d, J = 11 Hz, 3 H), −4.47 (s, 3H), 1.75 (s, 15H), 3.85 (d, J = 13.5 Hz, 3 H), 4.46 (d, J = 13.5 Hz, 3 H), 6.10 (s, 3H), 7.82 (s, 6H), 9.58 (s, 3H), 22.38 (s, 3H), 37.14 (s, 1H), 45.83 (s, 1H), 53.15 (s, 1H). IR (KBr): 2955, 2906, 2849, 1451, 1377, 1300, 1123, 1094, 1033, 813, 728, 694, 668.

(17) Crystallographic data for **2a**. Single crystals of **2a** are, at 203 K, triclinic, $P\bar{1}$, with a = 10.0200(5) Å, b = 13.4547(6) Å, c = 15.4750(7) Å, α = 85.099(1)°, β = 80.321(1)°, γ = 79.574(1)°, V = 2019.37(16) Å^3, Z = 4, D_{calc} = 1.327 Mg/m^3, for 7526 independent reflections, final R = 0.0310, R_w = 0.0794. Detailed information is available in the Supporting Information.

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Interestingly, there is no reaction when $(C_5Me_5)_2U({=}NPh)_2$ is heated in C_6D_6. The complex decomposes before any activation products are observed. This result gives a qualitative indication that electronic character of the N-bound ancillary ligand plays an important role in high-valent organoactinide complexes. Substitution of the electron-rich, though sterically demanding adamantyl group for the smaller, less electron-donating phenyl group significantly alters the imido reactivity. Efforts are under way to prepare other alkylimido analogues of **1** such as $(C_5Me_5)_2U({=}NR)_2$, where R is a less sterically demanding alkyl group, to investigate the influences of steric and electronic factors on the reactivity of the imido group.

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Supporting Information Available: Tables of crystal data, structure solution and refinements, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2a** are available free of charge via the Internet at http://pubs.acs.org.

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