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Synthesis and Structure of the First Uranium(VI) Organometallic Complex

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The chemistry of complexes of the d-transition elements containing organoimido functional groups constitutes a rapidly expanding area of research.[1] Examples of molecules containing multiple terminal imido functional groups now exist for representative elements from groups 5-8.[1,2] In contrast, f-metal terminal organoimido complexes are still relatively rare,[3] and examples of single actinide metal sites coordinated by greater than one imido ligand are unknown. On the basis of the stability of uranyl ion $(UO_2)^{2+}$, there appears to be no reason why the isoelectronic bis(organoimido) species should not be accessible.[4] Development of this chemistry has been hampered by the lack of synthetic routes to high-valent (V, VI) uranium complexes and by the relatively small number of ligands which have been demonstrated to stabilize these oxidation states.[3-5] Here we describe the synthesis and structural characterization of the first bis(organoimido) complex of uranium(VI). This species also represents the first complex of uranium(VI) supporting metal-carbon bonding in either a σ- or π-fashion.

As part of our studies of preparative routes to uranium organoimido complexes,[3a] we are examining generation of uranium imido functionalities by abstraction of an amido hydrogen by a leaving hydrocarbyl or amido ligand.[6] The room temperature reaction of red-orange $(C_5Me_5)_2U(CH_3)Cl$[7] with 1 equiv of $LiNHC_6H_5$ in diethyl ether for 12 h in the presence of 1 equiv of TMEDA results in the slow evolution of methane and the formation of a brown-orange solution. Following removal of the diethyl ether under reduced pressure, the residue is extracted with toluene, the extract is filtered through Celite, and the solvent is removed in vacuo. Treatment of the resulting red-brown oil with cold hexane yields $[Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl$ (**1**)[8] as a brown-orange powder in 75% yield (eq 1).[9]

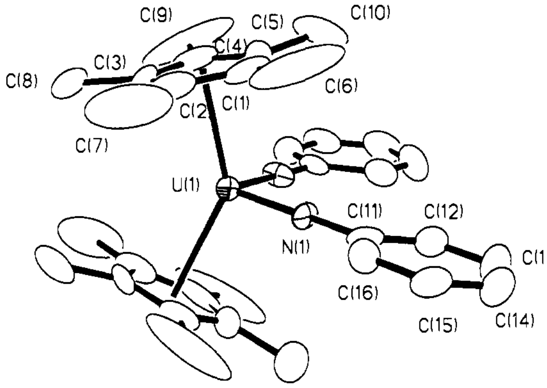

Figure 1. ORTEP drawing of $Cp^*_2U(NC_6H_5)_2$ (**2**), with atoms shown as 50% probability ellipsoids. Selected distances (Å) and angles (deg) for **2**: U(1)-N(1) = 1.952 (7), U(1)-N(1)-C(11) = 177.8 (6), N(1)-U(1)-N(1′) = 98.7 (4), Cp*(centroid)-U(1)-Cp* = 141.9.

$$(C_5Me_5)_2U(CH_3)Cl + 1LiNHC_6H_5 + TMEDA \xrightarrow[-CH_4]{(C_2H_5)_2O} \underset{\mathbf{1}}{[Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl} \quad (1)$$

The addition of 1 equiv of phenyl azide to a stirred solution of **1** in diethyl ether at room temperature results in a rapid color change from brown-orange to black-brown with the evolution of nitrogen.[3c] After 12 h the solvent is removed, yielding $(C_5Me_5)_2U(NC_6H_5)_2$ (**2**) as a black-green powder (85% yield) upon washing with cold hexane (eq 2).[10] Compound **2** is soluble in ether and aromatic solvents and exhibits only modest air and moisture sensitivity.

$$[Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl + 1N_3C_6H_5 \xrightarrow[-N_2]{(C_2H_5)_2O} \underset{\mathbf{2}}{(C_5Me_5)_2U(NC_6H_5)_2} \quad (2)$$

Compound **2** may be more directly prepared in high yield (80%) by the addition of 1-lithio-1,2-diphenylhydrazine to a stirred diethyl ether solution of $(C_5Me_5)_2U(CH_3)Cl$ at room temperature (eq 3). Evolution of methane is vigorous, and the solution color changes from the deep maroon of $(C_5Me_5)_2U(CH_3)Cl$ to the black-brown of **2** within ca. 15 min. The intermediacy of a U(IV) η^2-1,2-diphenylhydrazido(2−) species may be postulated, which subsequently undergoes N-N bond cleavage to form **2**. Other

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(9) $[Li(TMEDA)](C_5Me_5)_2U(NC_6H_5)Cl$ (**1**): ^1H NMR (250 MHz, C_6D_6, 25 °C) δ 39.55 (s, $\nu_{1/2}$ = 31 Hz, 2 H, meta), 30.45 (s, $\nu_{1/2}$ = 31 Hz, 2 H, ortho), 13.79 (s, $\nu_{1/2}$ = 31 Hz, 1 H, para), 4.82 (br, $\nu_{1/2}$ = 78 Hz, 4 H, $Me_2NC\mathit{H}_2C\mathit{H}_2NMe_2$), 3.29 (br, $\nu_{1/2}$ = 250 Hz, 12 H, $\mathit{Me}_2NCH_2CH_2N\mathit{Me}_2$), −1.27 (s, $\nu_{1/2}$ = 15 Hz, 30 H, $C_5\mathit{Me}_5$); IR (Nujol mull) 1288 (s), 1272 (vs), 1264 (vs), 1224 (m), 1188 (w), 1160 (s), 1148 (w), 1120 (m), 1092 (w), 1069 (w), 1064 (m), 1031 (m), 1016 (m), 1010 (m), 992 (s), 984 (w), 977 (w), 952 (m), 900 (s), 876 (m), 828 (w), 792 (s), 783 (w), 764 (s), 724 (m), 692 (s), 672 (w), 628 (s), 608 (m), 592 (w), 584 (m), 492 (m). Anal. Calcd for $C_{32}H_{51}N_3LiClU$: C, 50.68; H, 6.79; N, 5.54. Found: C, 51.06; H, 6.69; N, 5.17.

(10) $(C_5Me_5)_2U(NC_6H_5)_2$ (**2**): ^1H NMR (250 MHz, C_6D_6, 25 °C) δ 9.26 (t, 4 H, J_{HH} = 7.75 Hz, meta), 4.16 (s, 30 H, $C_5\mathit{Me}_5$), 2.82 (d, 4 H, J_{HH} = 7.46 Hz, ortho), 0.72 (t, 2 H, J_{HH} = 7.35 Hz, para); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): δ 181.2 (C_{phenyl}), 143.4 (C_{phenyl}), 136.5 (C_{ipso}/C_{ring}), 110.8 (C_{ipso}/C_{ring}), 109.7 (C_{phenyl}), 7.7 ($C_5\mathit{Me}_5$); IR (Nujol mull) 1273 (s), 1266 (s), 1252 (m), 1210 (vw), 1160 (m), 1142 (w), 1062 (m), 1014 (m), 992 (m), 905 (s), 889 (m), 860 (w), 819 (w), 756 (vs), 686 (vs), 601 (vw), 527 (s). Anal. Calcd for $C_{32}H_{40}N_2U$: C, 55.65; H, 5.84; N, 4.06. Found: C, 55.27; H, 6.06; N, 3.74.

0002-7863/92/1514-10068$03.00/0

coordination geometries of the 1,2-diphenylhydrazido(2−) ligand cannot be ruled out, however.[11]

$$(C_5Me_5)_2U(CH_3)Cl + 1LiN(C_6H_5)NH(C_6H_5) \xrightarrow[-CH_4]{(C_2H_5)_2O} \underset{\mathbf{2}}{(C_5Me_5)_2U(NC_6H_5)_2} \quad (3)$$

Single crystals of **2** were grown from a concentrated toluene solution at −40 °C, and the structure was determined from diffraction data collected at −80 °C (Figure 1).[12] In the solid state, **2** is shown to be monomeric with a pseudotetrahedral coordination environment about the uranium atom. The molecule lies on a 2-fold axis of symmetry and therefore possesses one unique organoimido group and one unique pentamethylcyclopentadienyl ring. The U–C_{ring} distances (U(1)–C_{ring} range = 2.718 (10)–2.746 (8) Å) are not appreciably shorter than those in structurally characterized bis(pentamethylcyclopentadienyl)uranium(IV) compounds,[13] as one might expect from the relative radii of U(IV) and U(VI).[14] This may be due to interligand repulsions, although there do not appear to be any unusually close contacts between methyl groups on the two pentamethylcyclopentadienyl rings. The Cp*(centroid)–U–Cp* angle is 141.9°, which is somewhat larger than values typically found in $Cp^*{}_2UX_2$ complexes.[13] The short uranium–nitrogen bond length (U(1)–N(1) = 1.952 (7) Å) and nearly linear U–N–C_{ipso} bond angle (U(1)–N(1)–C(11) = 177.8 (6)°) are consistent with the formulation of the ligands as organoimido groups. The uranium–nitrogen bond distance is similar to those previously determined for uranium(V) ($(MeC_5H_4)_3UNPh$: U–N = 2.019 (6) Å[3c]) and uranium(VI) ($[N(SiMe_3)_2]_3U(F)(NPh)$: U–N = 1.979 (8) Å[3a]) phenylimido complexes. The room temperature electronic absorption spectrum of **2**, recorded in toluene solution from 1500 to 300 nm, is also consistent with the assignment of a U(VI) metal center, with an absence of weak f → f transitions in the near IR. The unprecedented nonlinear (cis) orientation of the bis(imido)uranium unit (N(1)–U(1)–N(1′) = 98.7 (4)°) has no structural analogs among complexes of the isoelectronic uranyl ion, UO_2^{2+}, which have heretofore always been shown structurally and spectroscopically to be linear.[4]

The phenylimido ligands are nearly coplanar; the dihedral angle between the two phenyl rings is 6.7°. The rings rotate freely in solution, however. Only one set of phenyl ortho, meta, and para resonances is observed by ^1H and ^{13}C NMR spectroscopy at room temperature.[10] An unusual feature in the ^1H NMR spectrum of **2** is the positions of the phenylimido proton resonances at 9.26 (meta), 2.81 (ortho), and 0.72 (para), all of which are temperature invariant. We have previously reported similar chemical shifts in another U(VI) phenylimido complex.[3a] Two possible explanations have been offered for this behavior: (i) a high degree of ionic character in the metal–imide nitrogen bond is resonance delocalized to the ortho and para carbons, which, in turn shields the attached protons and shifts them to higher fields, and/or (ii) the uranium(VI) ion is behaving as a temperature independent paramagnet (TIP). We are currently examining the variable temperature magnetic behavior of **2**.

In summary, we report here the synthesis and structural characterization of the first complex of uranium(VI) displaying metal–carbon π-bonding; this is the only reported uranium(VI) organometallic complex. Further, this complex is the first example of a bis(organoimido) uranium(VI) analogue to the uranyl ion, UO_2^{2+}. The molecule displays an unusual nonlinear geometry of the two organoimido functional groups. Whether this arrangement is electronically or sterically mandated, some unusual differences in the electronic structure and reactivity of the bis(imido)- and dioxo–metal cores are likely to result. We are continuing our studies of the preparation and behavior of this new class of complexes.

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Supplementary Material Available: Tables of data collection constants, atomic positional parameters, anisotropic thermal parameters, selected bond lengths and angles, hydrogen atom positions, and summary of rejected reflections for **2** (10 pages); listing of observed and calculated structure factors for **2** (9 pages). Ordering information is given on any current masthead page.

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[12] Crystal data for **2**: monoclinic space group $C2/c$, a = 11.206 (3) Å, b = 15.303 (5) Å, c = 17.010 (5) Å, β = 103.93 (2)°, V = 2831.1 (14) $Å^3$, Z = 4, d_{calcd} = 1.620 g/cm^3. Data were collected at −80 °C utilizing Mo Kα radiation (λ = 0.71073 Å) and 2θ limits of 3−50°. Some data were rejected prior to data processing when it was determined that the diffracted beam intensity had been obscured by the nozzle of the low-temperature device. Remaining diffraction data were corrected for absorption, and the structure was solved by a combination of Patterson and Fourier techniques. Hydrogen atoms were placed in idealized positions; they were not refined anisotropically. Final residuals were R_F = 0.0483 and R_{wF} = 0.0631 for 2200 reflections with $F_o \geq 3\sigma(F_o)$.

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The Central Bond $^{13}C{=}^{13}C$ Isotope Effect for Superconductivity in High-T_c β^*-$(ET)_2I_3$ and Its Implications Regarding the Superconducting Pairing Mechanism

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We report a new study, based on dc magnetization measurements, of the superconducting isotope effect for ^{13}C-substitution in the central C=C atoms of ET [bis(ethylenedithio)tetrathiafulvalene] in β^*-$(ET)_2I_3$ [or β_H-$(ET)_2I_3$], the crystallographically ordered form of β-$(ET)_2I_3$ produced by pressure.[1] Merzhanov et al. recently reported[2] that this ^{13}C-substitution yields a "giant" isotope effect in resistive studies, wherein T_c = 8.0 ± 0.1 K

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