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Diuranium Inverted Sandwiches Involving Naphthalene and Cyclooctatetraene

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Discussions of bonding in the organometallic chemistry of uranium have appeared with increasing frequency since the seminal description of uranocene.[1,2] Delta bonds have been proposed to play a key role in stabilizing inverted sandwiches comprised of two uranium atoms bridged by a cyclic aromatic hydrocarbon ligand.[3] Examples to date of such inverted sandwiches involve benzene, toluene,[3] or cycloheptatrienyl[4] as a planar symmetrical bridging group. An ancillary ligand capable of supporting a broad range of arene-bridged compounds was targeted to facilitate structural and spectroscopic comparisons as a function of the bridging ligand. This communication reports the chemistry of a uranium trisketimide fragment that has allowed for the isolation of unique naphthalene- and cyclooctatetraene-bridged diuranium complexes.

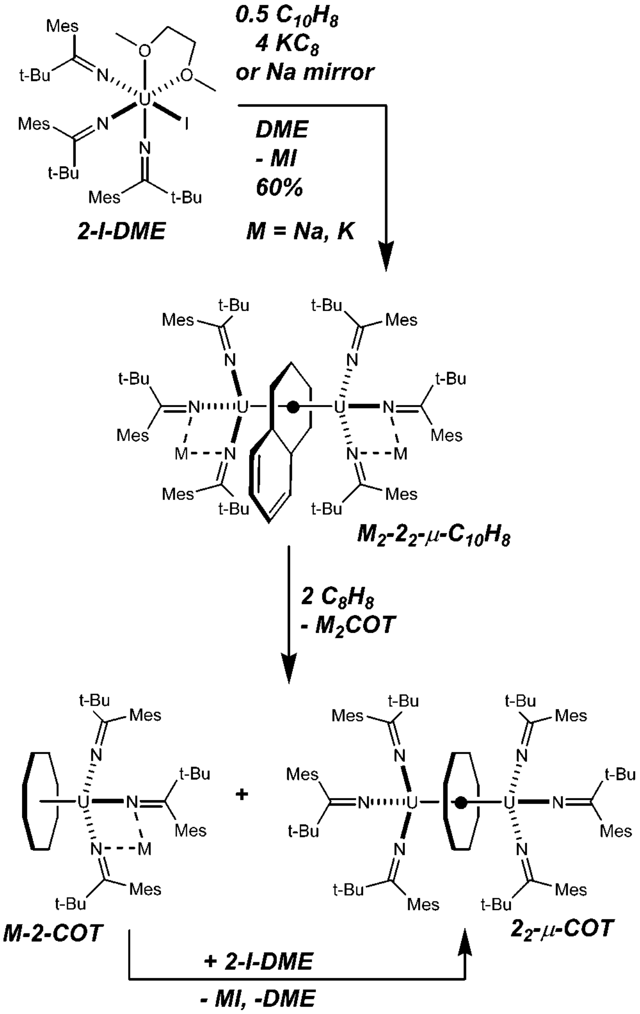
The previously described system $(\mu\text{-C}_7\text{H}_8)\text{U}_2(\text{N}[^t\text{Bu}]\text{Ar})_4$ (Ar = 3,5-$\text{C}_6\text{H}_3\text{Me}_2$, **$\mathbf{1_2}$-$\boldsymbol{\mu}$-$\mathbf{C_7H_8}$**)[3] evinces a two-legged piano stool coordination environment at uranium, one *N-tert*-butyl anilide ligand having been stripped from each uranium center during conversion from the uranium trisamide precursor, $\text{IU}(\text{N}[^t\text{Bu}]\text{Ar})_3$.[5] Since the synthesis involved treatment with excess KC_8[6] in the neat arene solvent, it is presumed that the stripped ligand was lost as its potassium salt. The new ketimide ligand ($\text{NC}[^t\text{Bu}]\text{Mes}$, Mes = 2,4,6-$\text{C}_6\text{H}_2\text{Me}_3$) employed in the present study allows for retention of three supporting ligands per uranium, giving rise to a three-legged piano stool geometry, and it allows also for incorporation of potassium ions as tight ion pairs. A further advance accorded by the implementation of ketimide ligands[7] is the ability to use dimethoxyethane (DME) solvent and stoichiometric amounts of a particular desired hydrocarbon ligand, naphthalene, in the present study.

Reaction of readily available $\text{UI}_3(\text{DME})_2$[8] with $\text{KNC}[^t\text{Bu}]\text{Mes}$ in DME led to the isolation of dark green-brown $\text{IU(DME)}(\text{NC}[^t\text{Bu}]\text{Mes})_3$ (**2-I-DME**), in 30% yield.[9] A single-crystal X-ray diffraction study of **2-I-DME** revealed that a molecule of DME coordinates to the uranium center in the pocket formed by the mesityl groups. The observed near-linear UNC angles (average 168.2(8)°)[10] are suggestive of significant π bonding between nitrogen and uranium, as are the UN distances, which are shorter on average by ca. 0.1 Å than those observed for related uranium amides.[3,5]

Treatment of **2-I-DME** with 4 equiv of KC_8 and 0.5 equiv of naphthalene in DME allowed the isolation of a naphthalene-bridged compound, $\text{K}_2(\mu\text{-}\eta^6,\eta^6\text{-C}_{10}\text{H}_8)[\text{U}(\text{NC}[^t\text{Bu}]\text{Mes})_3]_2$ (**$\mathbf{K_2}$-$\mathbf{2_2}$-$\boldsymbol{\mu}$-$\mathbf{C_{10}H_8}$**, Scheme 1) in 60% yield as a dark brown powder.

The most interesting structural feature of this compound is the coordination mode, μ-η^6,η^6, of the bridging naphthalene to the uranium centers[11] (Figure 1), reminiscent of the coordination mode of toluene in compound **$\mathbf{1_2}$-$\boldsymbol{\mu}$-$\mathbf{C_7H_8}$**. The twelve U−C distances are quite short, varying from 2.565(11) Å to 2.749(10) Å. The longer bonds are registered to the two carbon atoms fusing the two six-membered rings, a fact understandable inasmuch as the LUMO of naphthalene lacks any orbital contributions from these atoms.[12]

Scheme 1



The C−C distances in the bound ring are regular and not alternating (average of 1.443(6) Å), consistent with the aromatic character expected for that ring, while in the pendant ring a diene-like character is suggested by bond alternation (1.470(16), 1.319(17), 1.467(18) 1.381(15), and 1.395(15) Å). Each potassium ion is clasped by a complement of two mesityl rings, the pendant portion of the naphthalene ligand, and two ketimide nitrogen atoms in a side-on fashion. Complexation of the potassium ions in this way provides them with a near-spherical shroud of electron density, revealing **$[\mathbf{2_2}$-$\boldsymbol{\mu}$-$\mathbf{C_{10}H_8}]^{2-}$** to be an excellent alkali-metal cation receptor. Furthermore, internalizing the positive ions permits

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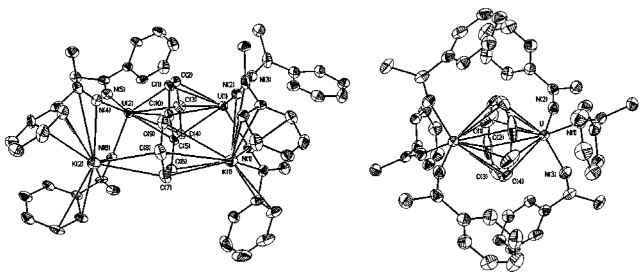

Figure 1. Structural drawings of **K$_2$-2$_2$-μ-C$_{10}$H$_8$** (left) and **2$_2$-μ-COT** (right) with thermal ellipsoids at the 35% probability level. Methyl groups have been omitted for clarity.

the system to present to its exterior solely lipophilic residues, accounting for the observed high solubility in hydrocarbon solvents.[13] It is worth mentioning that neither the uranium nor the potassium centers retain DME as a coordinated solvent molecule. The U−N distances are elongated by about 0.1 Å with respect to those in precursor **2-I-DME**, consistent with an increase in formal negative charge (decrease in oxidation state) at uranium.

The corresponding sodium derivative, Na$_2$(μ-η^6,η^6-C$_{10}$H$_8$)[U(NC[^{t}Bu]Mes)$_3$]$_2$ **Na$_2$-2$_2$-μ-C$_{10}$H$_8$**, was obtained as dark green-brown crystals in 40% yield by reducing **2-I-DME** over a sodium mirror in tetrahydrofuran (THF) in the presence of 0.6 equiv of naphthalene. A preliminary X-ray crystal structure indicated that **Na$_2$-2$_2$-μ-C$_{10}$H$_8$** crystallizes with two THF molecules coordinated to each sodium center, while ^{1}H NMR spectroscopic data are consistent with desolvation after vacuum drying for several hours.

Investigation of the naphthalene-bridged systems by ^{1}H NMR spectroscopy revealed fluxional behavior, a single ketimide ligand environment being observed. For both **M$_2$-2$_2$-μ-C$_{10}$H$_8$** (M = Na, K) the corresponding monodeuterated and fully deuterated naphthalene-bridged compounds were prepared with α-naphthalene-d_1 and naphthalene-d_8. The solution structure is consistent with that observed in the solid state with respect to the naphthalene coordination, since four ^{2}H NMR signals are observed for the d_8 derivative. Combining the results of 2D NMR correlation experiments with the line width of the signals in the ^{1}H NMR spectrum, and with the signals found in the ^{2}H NMR spectrum of **Na$_2$-2$_2$-μ-C$_{10}$H$_7$D(α)**, the peaks at 79.2 (β-H) and −128.9 (α-H) ppm were assigned to the deuterons of the ring bridging the two uranium centers, while the peaks at −28.9 (α-H) and −36.5 (β-H) ppm were assigned to the deuterons of the dangling ring (see the Supporting Information for details and assignments for the potassium salt).

Treatment of **M$_2$-2$_2$-μ-C$_{10}$H$_8$** (M = Na, K) with 2 equiv of 1,3,5,7-cyclooctatetraene afforded a mixture of two products (Scheme 1). Compounds K[(COT)U(NC[^{t}Bu]Mes)$_3$] (**K-2-COT**) and [Na(S)][(COT)U(NC[^{t}Bu]Mes)$_3$] (**Na-2-COT**, S = Et$_2$O) are insoluble in pentane, facilitating their separation from the neutral coproduct **2$_2$-μ-COT**, (μ-η^8,η^8-COT)U$_2$(NC[^{t}Bu]Mes)$_6$ (Figure 1). The ratio in which the two compounds are formed seems independent of the solvent employed. If **Na$_2$-2$_2$-μ-C$_{10}$H$_8$** is used the two compounds form in a 1:1 ratio and **2$_2$-μ-COT** may be isolated in 35% yield. When **K$_2$-2$_2$-μ-C$_{10}$H$_8$** is used as a starting material for the reaction with 1,3,5,7-cyclooctatetraene, almost only **K-2-COT** is formed. Thus, the **[2-COT]**$^-$ anion is easiest to isolate as its potassium salt (diethyl ether, 60% yield). Interestingly, compound **2$_2$-μ-COT** can be assembled independently in 90% yield by salt elimination upon reaction of **M-2-COT** with iodide **2-I-DME**.

Reactions forming **2$_2$-μ-COT** we refer to as “inverting uranocene” because they result in a C$_8$H$_8$ ring being sandwiched symmetrically between two uranium atoms instead of the reverse.

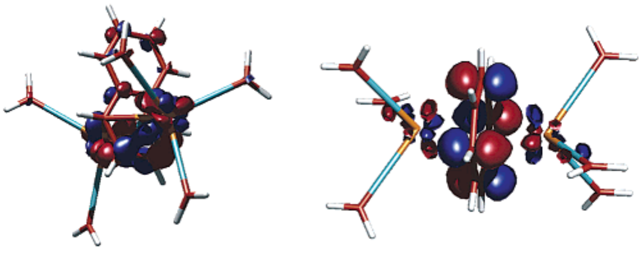

Figure 2. For both complexes [(μ-C$_{10}$H$_8$)U$_2$(NCH$_2$)$_6$]$^{2-}$ and [(μ-C$_8$H$_8$)U$_2$(NCH$_2$)$_6$], electrons 5−8 are involved in covalent δ interactions between the metals and the ring, the electrons being numbered in sequence of decreasing energy. Calculations were spin unrestricted such that the orbital containing electron 5 is pictured at the left for [(μ-C$_{10}$H$_8$)U$_2$(NCH$_2$)$_6$]$^{2-}$ and at the right for [(μ-C$_8$H$_8$)U$_2$(NCH$_2$)$_6$].

Structurally related systems (with presumably far greater ionic character) exist for samarium, europium, and ytterbium.[14] Compounds **Na-2-COT** and **2$_2$-μ-COT** (see the Supporting Information for pictures and details) have been crystallographically characterized. The U−C$_{\text{arene}}$ distance in compound **2$_2$-μ-COT** is longer on average than that in its naphthalene counterpart **K$_2$-2$_2$-μ-C$_{10}$H$_8$** (2.822 vs 2.634 Å), in accord with bonding considerations (Figure 2) that indicate poorer covalent overlap in the former.

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Supporting Information Available: Details of the X-ray crystallographic studies, DFT calculations, synthetic procedures and characterization data for the reported compounds (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Yield was calculated with respect to the starting material, UI$_3$(DME)$_2$. The low yield is attributed to disproportionation of the starting U(III) compound and high lipophilicity of the desired material.

(10) See SI for details of the X-ray crystal structure of **2-I-DME**.

(11) A search of the Cambridge Crystallographic Database (CSD) revealed no other examples of this coordination mode for naphthalene. This is true both for transition metals and actinide elements.

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