Heterodinuclear Uranium/Molybdenum Dinitrogen Complexes

Aaron L. Odom, Polly L. Arnold, and
Christopher C. Cummins*

Department of Chemistry Room 2-227
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139-4307

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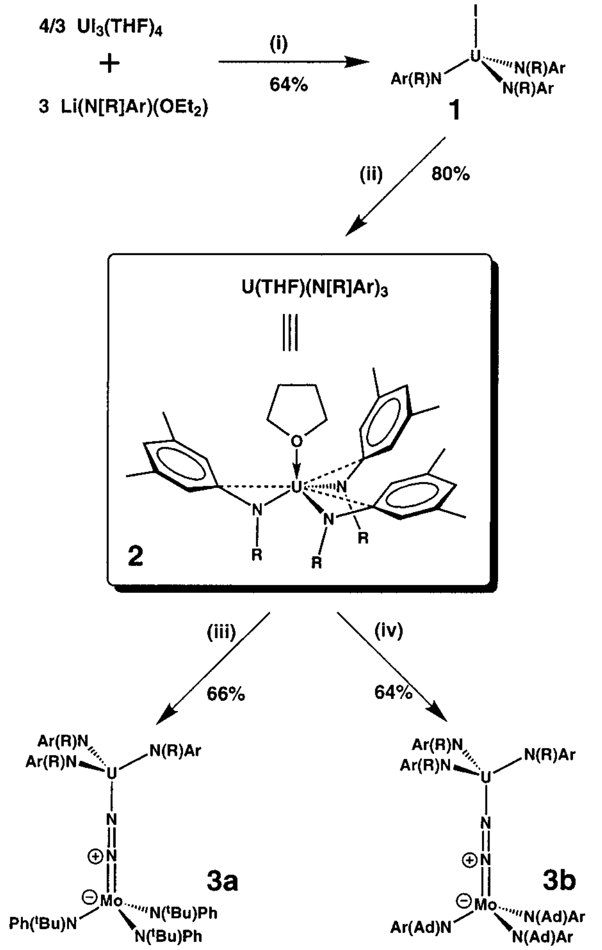
Binding of the prototypical π-acid CO by molecular uranium complexes has been limited to spectroscopic observation[1] and a single recent crystal structure.[2] This being the case, it is not surprising that little is known about the interaction of uranium complexes with dinitrogen. The most important work in the latter area to date comprises the very recent isolation and structural characterization of a diuranium complex with N_2 as an η^2 (side-on) bridging ligand;[3] the supporting ligands used were of the triamidoamine variety.[4] As reported herein, uranium can be decorated with *N-tert*-butylanilide ligands and coaxed into an end-on interaction with dinitrogen. The key complexes reported here are the first heterodinuclear complexes with a $U-N_2$ interaction.

Our investigation takes advantage of the versatile starting material, $U(I)_3(THF)_4$, which has been shown to represent a convenient entry into uranium(III) chemistry.[5] The major product resulting from interaction of $Li(N[R]Ar)(OEt_2)$[6] with $U(I)_3(THF)_4$ was found to be the yellow uranium(IV) species $U(I)(N[R]Ar)_3$ (**1**). The optimum stoichiometry (Scheme 1) assumes that reduction of one sacrificial equiv of U^{3+} to U^0 occurs en route to formation of **1**. NMR data for **1** recorded in C_6H_6 at 25 °C are indicative of a single ligand environment.

With the objective of synthesizing a homoleptic amide of uranium(III),[7] **1** was treated in THF with 1% Na/Hg (Scheme 1). The reaction resulted in high-yield formation of the black THF adduct $U(THF)(N[R]Ar)_3$ (**2**). Characterization data are in accord with the compound's formulation as a monomeric uranium(III) derivative with a single $-N(R)Ar$ ligand environment at 25 °C.

X-ray crystallography confirmed the formulation of **2** (Figure 1). A rare example of a crystallographically characterized uranium(III) amide, the U−N bond lengths in **2** (av 2.320 Å) are ~0.04 Å shorter than the terminal U−N bonds in $[U(N[SiMe_3]_2)_2(\mu\text{-NHMes})]_2$.[8] The electrophilic nature of low-coordinate uranium(III) is reflected in the structure of **2** by close $U\cdots C_{ipso}$ contacts of ~2.9 Å, as expected for uranium(III)−arene π-complexation.[9] Interaction of *N-tert*-butylanilide C_{ipso} carbons with electrophilic metal centers is precedented.[10] In addition, the 2.518(8) Å U−O distance in $U(THF)(N[R]Ar)_3$ is shorter by ~0.03 Å than that in $Cp_3U(THF)$.[11] A striking aspect of the solid-state conformation of **2** is the location of the THF ligand in the arene "bowl", rather than in the *tert*-butyl "pocket" as observed frequently for transition-metal analogues.[12]

Scheme 1[a]



[a] Key: (i) C_7H_8, −90 to 0 °C, −3 LiI, −"U^0"; (ii) 4 equiv Na/Hg (1% w/w), THF, 20 min; (iii) $Mo(N[t\text{-}Bu]Ph)_3$, N_2 (1 atm), 25 °C, C_7H_8, −THF; (iv) $Mo(N[Ad]Ar)_3$, N_2 (1 atm), 25 °C, C_7H_8, −THF.

As **2** by itself does not evince any detectable reactivity toward N_2, it seemed plausible that the compound might participate in formation of heterodinuclear N_2 complexes. Accordingly, stirring a 1:1 mixture of **2** and $Mo(N[t\text{-}Bu]Ph)_3$[13] in toluene under N_2 (1 atm) led over 20 min to quantitative formation of the desired $U(\mu\text{-}N_2)Mo$ complex **3a** (Scheme 1), which was isolated in 66% yield as an orange solid.[14] A plausible rationale for the observed result is that the putative dinitrogen complex $(N_2)Mo(N[t\text{-}Bu]Ph)_3$ is more efficiently trapped by **2** than by $Mo(N[t\text{-}Bu]Ph)_3$. Reactions of $Mo(N[t\text{-}Bu]Ph)_3$ and derivatives with dinitrogen have been described in detail.[13]

Inspection of the IR spectrum of paramagnetic **3a** did not reveal an obvious band, thus providing suggestive *negative* evidence

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[14] Characterization data, synthetic protocols, and details of the X-ray investigations are deposited as Supporting Information.

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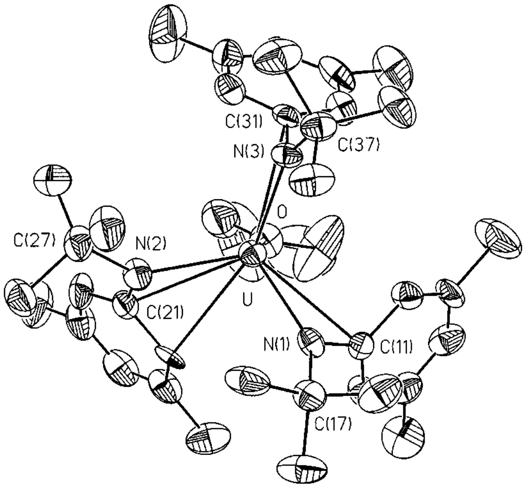

Figure 1. Structural drawing of U(THF)(N[R]Ar)$_3$ (**2**) with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): U−N(1), 2.295(10); U−N(3), 2.306(9); U−N(2), 2.361(9); U−O, 2.518(8); U−C(31), 2.886(12); U−C(11), 2.889(12); U−C(21), 2.980(12); U−C(22), 3.027(11); N(1)−U−N(3), 108.0(3); N(1)−U−N(2), 107.9(3); N(3)−U−N(2), 112.1(3); N(1)−U−O, 115.1(3); N(3)−U−O, 108.8(3); N(2)−U−O, 104.9(3); C(31)−U−C(11), 116.4(4); C(31)−U−C(21), 123.6(4); C(11)−U−C(21), 116.1(4); O−U−N(1)−C(17), −149.05 (1.09); O−U−N(2)−C(27), −126.76 (1.20); O−U−N(3)−C(37), −151.15 (1.16).

for a side-on bonding mode for the N$_2$ ligand. A second derivative **3b**, containing a more sterically encumbered Mo center, was therefore prepared by mixing **2** with Mo(N[Ad]Ar)$_3$ (Ad = 1-adamantyl) in toluene under N$_2$, as in the synthesis of **3a**. It was postulated that the more hindered nature of the Mo center in **3b** would favor an end-on, linear bridging bonding mode for the N$_2$ ligand. Accordingly, a prominent ν_{NN} band was observed for **3b** at 1568 cm^{-1}, the band shifting to 1527 cm^{-1} for **3b-^{15}N$_2$**. Upon subsequent synthesis of **3a-^{15}N$_2$** and examination of its IR spectrum, ν_{NN} was located at 1547 cm^{-1}, such that the lack of observation of ν_{NN} for unlabeled **3a** was finally attributed to overlap with prominent amide aryl ring ν_{CC} modes. By way of comparison, the previously characterized complex (μ-N$_2$)[Mo(N[R]Ar)$_3$]$_2$ has its ν_{NN} at 1630 cm^{-1}.[13]

Further corroboration of the end-on bridging bonding mode for the N$_2$ ligand in complexes **3** comes from an X-ray structure determination for **3a** (Figure 2).[14] Both metal centers in the complex display pseudotetrahedral coordination, and they are conformationally similar in that the N$_2$ ligand resides inside a "cage" consisting of the six *tert*-butyl groups. Only one U$\cdots$C$_{ipso}$ interaction is in evidence, contrasting with the situation for **2** and consistent with a higher formal oxidation state for the U center in **3a**. The smaller radius of uranium in **3a** vis-à-vis **2** is reflected in shorter U−N$_{amide}$ distances (av 2.257 Å). Substantial reduction of the N$_2$ molecule is indicated by the N−N distance of 1.232(11) Å, longer by 0.13 Å than that in free dinitrogen. Some degree of multiple bonding between N(7) and uranium is perhaps indicated, the U−N(7) distance being nominally shorter than the three U−N$_{amide}$ distances.

The structure of **3b**, which was also determined by X-ray crystallography, is quite similar to that of **3a** with respect to overall conformation and metrical parameters.[14]

The valence-bond resonance structure depicted for compounds **3** in Scheme 1 is inferred from the crystal structure data. It implies a formal oxidation state of +4 for both metals, with molybdenum acting as the more effective π-donor to the complexed N$_2$ ligand. Reductive cleavage of N$_2$ to two nitrides requires six electrons, which could in principle be supplied by Mo^{3+} in conjunction with U^{3+}, as in the reactions leading to complexes **3**. Complexes **3** appear to be thermally stable, however, a fact possibly reflective of the relative difficulty of accessing uranium(VI) in the absence of oxo or fluorine ligands. Terminal nitrides of uranium are not yet known in isolable complexes,[15] although uranium(V) and -(VI) imido complexes are documented.[16]

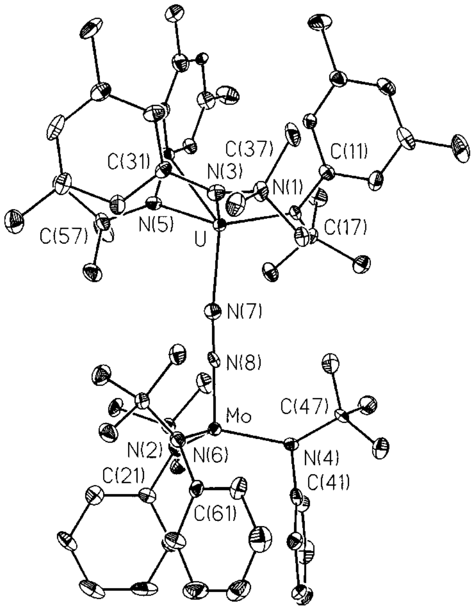

Figure 2. Structural drawing of (Ph[*t*-Bu]N)$_3$Mo(μ-N$_2$)U(N[R]Ar)$_3$ (**3a**) with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): U−N(7), 2.220(9); U−N(5), 2.249(8); U−N(1), 2.254(8); U−N(3), 2.267(8); U−C(51), 2.893(10); Mo−N(8), 1.773(8); Mo−N(4), 1.978(8); Mo−N(6), 1.976(8); Mo−N(2), 1.978(8); N(7)−N(8), 1.232(11); N(8)−N(7)−U, 173.8(7); N(7)−N(8)−Mo, 179.1(7); N(7)−U−N(5), 104.4(3); N(7)−U−N(1), 104.5(3); N(5)−U−N(1), 111.4(3); N(7)−U−N(3), 104.2(3); N(5)−U−N(3), 116.1(3); N(1)−U−N(3), 114.7(3); N(8)−Mo−N(4), 102.1(3); N(8)−Mo−N(6), 98.1(4); N(4)−Mo−N(6), 117.6(3); N(8)−Mo−N(2), 103.8(4); N(4)−Mo−N(2), 114.2(3); N(6)−Mo−N(2), 116.9(3).

Further reactivity studies involving **2** are underway. Among other things, it will be of interest to assess the lability of the THF ligand in **2** and to understand in detail the mechanism of formation of complexes **3**.

Note Added in Proof: Stewart and Andersen have determined the structure of U[N(SiMe$_3$)$_2$]$_3$.[17]

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Supporting Information Available: Synthesis and characterization data for all new complexes and X-ray details for complexes **2**, **3a**, and **3b** (13 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available via the Web only. See any current masthead page for ordering information and Web access instructions.

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