

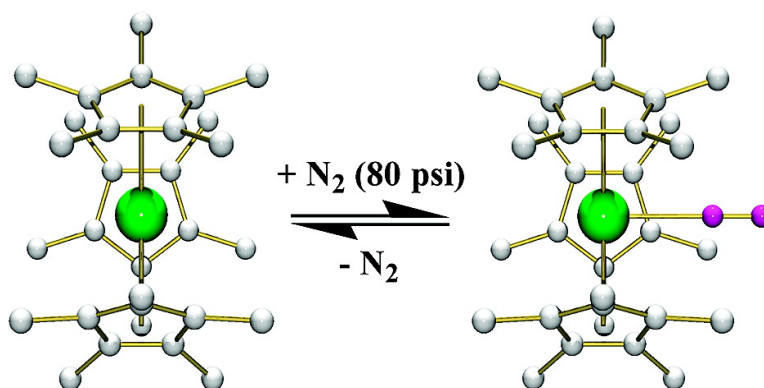
Communication

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A Monometallic f Element Complex of Dinitrogen: $(C_5Me_5)_3U(\eta^1-N_2)$

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The synthesis of sterically crowded $(C_5Me_5)_3M$ complexes has shown that it is possible to construct an extensive series of organometallic compounds in which all of the metal ligand bonds are unusually long.¹ For example, each Sm– $C(C_5Me_5)$ distance in $(C_5Me_5)_3Sm$ is 0.05–0.15 Å longer than conventional Sm– $C(C_5Me_5)$ lengths, and the 120° ligand cone angles are 10–20° smaller than normal. These long-bond organometallics also display unusual C_5Me_5 reactivity, including $(C_5Me_5)^{-1}/(C_5Me_5)$ sterically induced reduction and η^1 -alkyl-like insertion, ethylene polymerization, hydrogenolysis, and THF ring opening.¹ Access to this type of C_5Me_5 reactivity is apparently very sensitive to the steric crowding. For example, closely related compounds with normal bond lengths, such as $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$,² display none of the unusual reactivity of $(C_5Me_5)_3Sm$.³

The situation is more complicated with $(C_5Me_5)_3U$, **1**,^{4,5} and $(C_5Me_4H)_3U$, **2**.⁶ $(C_5Me_5)_3U$ participates in polymerization and reduction reactions, but analogous reactions have not been reported for **2**. However, **1** and **2** react similarly with CO to make the only crystallographically characterizable carbonyl complexes of ν elements, $(C_5Me_4R)_3U(CO)$ (R = H, Me).^{6–9} The latter complexes differ both in stability and structure. $(C_5Me_5)_3U(CO)$ rigorously retains the 120° cnt–U–cnt angles of **1** (cnt = C_5Me_4R ring centroid) and has unusual 90° cnt–U–C(CO) angles,⁸ while the more stable $(C_5Me_4H)_3U(CO)$ is pseudo-tetrahedral (cnt–U–cnt = 118–120°, cnt–U–C(CO) = 91.1–95.5°).^{6,7}

To explore further the factors that differentiate the reaction chemistry of **1** and **2**, we have compared their reactivity with THF, a common neutral donor for f elements,¹⁰ and N_2 , a nontraditional ligand for f elements^{11–18} that is similar to CO. This has resulted in the first example of an f element complex binding a formally neutral N_2 ligand end-on.

THF reactivity was initially studied because sterically crowded $(C_5Me_5)_3M$ complexes ring open this ether to form $(C_5Me_5)_2M-[O(CH_2)_4C_5Me_5](THF)$ ^{1,19} while less crowded systems form THF adducts, e.g., $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)(THF)$ ² and $(C_5H_5)_3U(THF)$.²⁰ Although the ¹H NMR spectra of **1** and **2** in C_6D_6 are unchanged upon addition of 1 equiv of THF, both compounds react in neat THF. **1** reacts irreversibly to form a product that has not yet been crystallographically characterized, but GC–MS analysis of its hydrolysis product, $HO(CH_2)_4C_5Me_5$, is consistent with THF ring opening. In contrast, complex **2** crystallizes from THF as the solvate $(C_5Me_4H)_3U(THF)$, **3**.²¹ The THF coordination is reversible: **3** loses THF quantitatively in C_6D_6 forming **2** (eq 1).

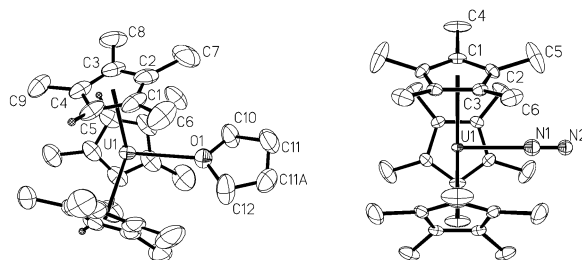
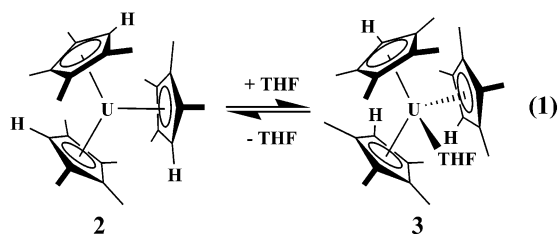
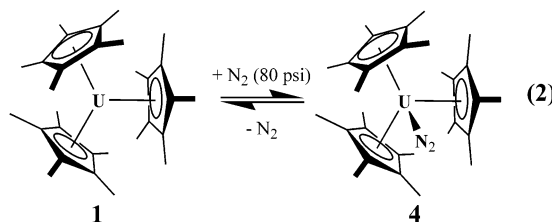


Figure 1. Thermal ellipsoid plots, drawn at 50%, of $(C_5Me_4H)_3U(THF)$, **3**, and $(C_5Me_5)_3U(\eta^1-N_2)$, **4**, showing the pseudo-tetrahedral C_5Me_4H vs trigonal C_5Me_5 ring arrangement in the $(C_5Me_4R)_3UL$ complexes. The disordered portions of the THF and the N_2 ligands are omitted for clarity.

X-ray analysis of **3** revealed a pseudo-tetrahedral geometry (Figure 1) (100.4° cnt–U–O(THF), 116.8° cnt–U–cnt) similar to that of $(C_5Me_4H)_3U(CO)$ ^{6,7} and $(C_5H_5)_3U(THF)$,²⁰ i.e., the C_5Me_4H rings bend back from the trigonal arrangement in **2** to accommodate the THF. The ring hydrogens are tipped away from the THF, which is located on a 3-fold rotation axis and is therefore disordered. The 2.650(6) Å U–O(THF) distance in **3** is significantly longer than the 2.55(1) Å U–O(THF) bond in the less substituted $(C_5H_5)_3U(THF)$.²⁰ Surprisingly, **3** has a 2.597 Å U–cnt distance which is similar to that in $(C_5Me_5)_3U$ (2.581 Å).⁴ Such crowding could make **3** as reactive as $(C_5Me_5)_3U$ ^{4,5} were it not for the facile THF desolvation. Additionally, **3** may be less reactive since it retains one normal U–C(C_5Me_4H) bond per ring, 2.734(4) Å in length, involving the H-substituted C(5) ring carbon.^{22–28}

Although neutral N_2 is an unlikely ligand for f elements, it was explored with **1** and **2** since they both form complexes with the similarly cylindrical CO.^{6–8} As with 1 equiv of THF, **1** and **2** show no obvious reactivity with N_2 (1 atm). However, solutions of **1** under N_2 at 80 psi slightly darken and produce hexagonal crystals of $(C_5Me_5)_3U(\eta^1-N_2)$, **4** (eq 2).²¹



As shown in Figure 1, N_2 coordinates end-on in **4**. Although terminal end-on binding of N_2 to transition metals is well documented,²⁹ it has never, to our knowledge, been observed in molecular f element complexes.³⁰ In fact, **4** appears to be the first monometallic f element complex of N_2 of any kind. N_2 units in f element complexes are most commonly found as $M_2(\mu-\eta^2:\eta^2-N_2)$ moieties involving $(N_2)^{2-}$.^{11–18} The three U/ N_2 complexes in the literature are $[U\{N(CH_2CH_2NSi^tBuMe_2)_3\}]_2(\mu-\eta^2:\eta^2-N_2)$ (**5**),¹³ $[U(C_5Me_5)(C_8H_4\{Si^tPr_3-1,4\}_2)]_2(\mu-\eta^2:\eta^2-N_2)$ (**6**),¹⁶ and $([Ph]^tBuN)_3Mo-$

(μ - η^1 : η^1 -N₂)U(N^tBu[3,5-C₆H₃Me₂])₃ (**7**),¹⁴ the closest structural analogue of **4** that has Mo and U bridged by (N₂)²⁻.

As in all other isolated (C₅Me₅)₃ML (M = U and L = F,³¹ Cl,³¹ CO⁸ or M = Th and L = H³²) complexes, the cnt-U-cnt angles in **4** are rigorously 120°, the cnt-U-N(N₂) angle is 90°, and the U-N-N angle is 180°. The unit cells of **1**, (C₅Me₅)₃ML, and **4** are indistinguishable. Also typical of the (C₅Me₅)₃ML complexes is that L, N₂ in this case, is disordered over the mirror plane that bisects the C₅Me₅ rings. Rearrangement of the rings to the pseudo-tetrahedral geometry of **3**, as with all crystallographically characterized (C₅Me₄H)₃UL' complexes (L' = Cl,³³ CN,⁶ CNC₆H₄-p-OMe,⁶ CO^{6,7}) documented in the CCDC database, is apparently not favored by the penta-substituted C₅Me₅ ring system.

The bond distances in **4** are similar to those in the other (C₅-Me₅)₃ML molecules: the 2.823(2)–2.927(4) Å U–C(C₅Me₅) distances (2.588 Å U–cnt) are longer than normal.^{22–28} The 2.492–(10) Å U–N(N₂) distance is comparable to the 2.485(9) Å U–C(CO) distance in (C₅Me₅)₃U(CO) and is longer than the 2.39–2.44 Å U–N(μ - η^2 : η^2 -N₂) distances in **5**¹³ and **6**¹⁶ and the 2.220(9) Å U–N(N₂)²⁻ distance in **7**.¹⁴ The 1.120(14) Å N–N distance is indistinguishable from the corresponding distance in both free N₂, 1.0975 Å,²⁹ and **5**, 1.097(7) Å.¹³ **4** has a shorter N–N bond length than the 1.23(1) Å distances in **6** and **7**.^{16,14}

The binding of N₂ to uranium in **4** is reversible: i.e., when the pressure is lowered to 1 atm, C₆D₆ solutions of **4** release N₂, quantitatively regenerating **1**. In contrast, solutions of (C₅Me₅)₃U(CO) are stable for hours under Ar or vacuum.⁸ Crystals of **4** are stable enough to reveal a 2207 cm⁻¹ IR absorption (KBr). This is assigned to the NN stretch since the ¹⁵N₂ analogue of **4** has an absorption at 2134 cm⁻¹ (predicted 2132 cm⁻¹). The ν (N₂) frequency of **4** is only slightly lower than that of free N₂, ν (N₂) = 2331 cm⁻¹ (Raman).²⁹ For comparison, the N₂²⁻ unit in **7** has a ν (N₂) = 1568 cm⁻¹. The 124 cm⁻¹ reduction of ν (N₂) in **4** from free N₂ can be compared with the 221 cm⁻¹ reduction of ν (CO) in (C₅Me₅)₃U(CO) from free CO.⁸ This is consistent with the relative stability of **4** vs (C₅Me₅)₃U(CO). Hydrolysis of a solid sample of ¹⁵N₂-enriched **4** formed a gas with a molecular weight of 30 by GC–MS.

The reaction of **2** with dinitrogen was also examined at high pressures since better binding by (C₅Me₄H)₃U might be expected based on comparisons between (C₅Me₄H)₃U(CO) and (C₅Me₅)₃U(CO).^{6–8} However, only (C₅Me₅)₃U crystallized from saturated solutions of **2** under 80 psi of N₂. This may be a crystallization problem since (C₅Me₄H)₃U is less soluble than (C₅Me₅)₃U and may crystallize before the alleged “(C₅Me₄H)₃U(N₂)” complex can be isolated. Alternatively, this difference between **1** and **2** may be related to the ligand reorganization which typically accompanies formation of (C₅Me₄H)₃UL' complexes and is not necessary in the C₅Me₅ system. The importance of ligand reorganization in U/N₂ chemistry has been described.^{33,34}

The isolation of **4** shows that with the appropriate ligand environment, end-on dinitrogen coordination is possible for f elements just as in transition metal chemistry. It is ironic that this end-on coordination was first identified with (C₅Me₅)₃U, a molecule already so sterically crowded that additional coordination is not expected to be favored.

Given the existence of **4**, it is likely that dinitrogen interactions with f elements occur in other coordination environments. Hence, f element reactions in noncoordinating solvents may be influenced by the “inert” atmosphere under which they were conducted. Reactions previously done under N₂ may have involved an undetected extra coordination that might not have occurred under Ar. In some cases, it may be worthwhile to reexamine under Ar

the reactions which did not proceed as expected under N₂. The isolation of **4** also has interesting implications for the recently discovered formation of [(Me₃Si)₂N]₂(THF)Ln₂(N₂) complexes from K/Ln[N(SiMe₃)₂]₃ precursors, a reaction which could involve “[Me₃Si)₂N]₃Ln(N₂)” intermediates.¹⁸

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Supporting Information Available: Experimental details, X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles for **3** and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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