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Reversible Binding and Reduction of Dinitrogen by a Uranium(III) Pentalene Complex

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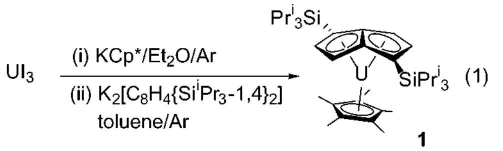
The binding and activation of dinitrogen by well-defined molecular complexes is an area of considerable current interest.[1] While N_2 coordination, reduction, and cleavage are all well-established for transition-metal systems, examples of such behavior for the actinide elements is extremely uncommon. Scott has reported a binuclear, U(III) triamidoamine complex containing a side-on bridging N_2 ligand in which the N−N bond length is essentially unperturbed from that in free N_2.[2] The only other example is the heterobimetallic U−Mo compound of Cummins, also supported by amide-type ligands, which contains a bridging, linear N_2^{2-} (diazenido) ligand.[3] We have recently developed the synthesis of the silylated pentalene dianion $C_8H_4\{Si^iPr_3\text{-}1,4\}_2^{2-}$ as a ligand for organo-*f*-element chemistry,[4] and given the ability of tris(cyclopentadienyl)uranium(III) complexes to bind CO,[5] we were encouraged to investigate the synthesis and reactivity of uranium(III) pentalene derivatives. In this work we report the preparation of the mixed-sandwich U(III) complex $[U(\eta\text{-}Cp^*)(\eta\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)]$ and its ability to reversibly bind and reduce dinitrogen to afford a binuclear U(IV) complex, which contains a bridging, sideways-bound N_2^{2-} ligand.

$[UI_3(THF)_4]$ is a useful starting material for U(III) chemistry;[6] however, since we wished to prepare U(III) pentalene complexes in the absence of strong donor ligands for subsequent reactions with small molecules, base-free UI_3 was employed in the present work. The latter may be conveniently prepared by reaction of U turnings with 1.5 equiv of HgI_2 in a sealed tube at 320 °C, in a modification of the method of Corbett for the synthesis of lanthanide triodides.[7] The reaction of UI_3 with 1 equiv of KCp* in diethyl ether affords a dark-green material which we assumed to be $\{UCp^*I_2\}_n$, or an etherate thereof. This was not isolated but reacted directly with $K_2[C_8H_4\{Si^iPr_3\text{-}1,4\}_2]$ in toluene under argon to afford purple-black, crystalline $[U(\eta\text{-}Cp^*)(\eta\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)]$ **1** in moderate (40%) yield after workup (see eq 1).[8]



Crystals of **1** suitable for X-ray diffraction studies were grown from hexane at −20 °C under argon, and the molecular structure is shown in Figure 1.[9]

1 adopts a slightly bent sandwich structure, in which the M1−U−M2 angle is 170.1° where M1 and M2 are the centroid of the Cp* ring and the midpoint of the pentalene (bridgehead) C4−C5 bond, respectively. The fold angle of the pentalene ring about the latter bond is 26°, compared with that of 24° in the more sterically congested Th(IV) complex $[Th(\eta\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)_2]$.[10] The U−C1 (2.733(7) Å), U−C3 (2.721(7) Å), U−C6 (2.683(7) Å), and U−C8 (2.722(7) Å) bond distances (which constitute the major, δ-symmetry bonding interaction in actinide pentalene complexes[11]) in **1** are correspondingly slightly shorter than those in $[Th(\eta\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)_2]$ (2.797(11), 2.748(10), 2.748(10), and 2.797(11) Å). The U−Cp* ring carbon distances lie in the range 2.734(8)−2.766(7) Å, comparable to those found in [UCp*(COT)(THF)] (average 2.752 Å).[12]

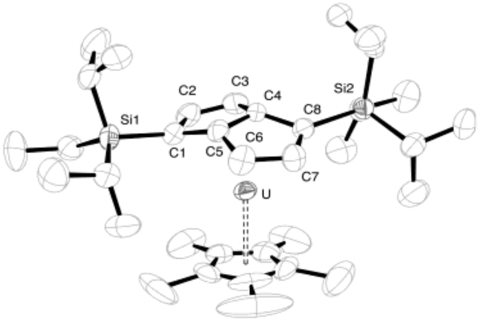


Figure 1. Molecular structure of **1** (thermal ellipsoids at 50%).

Both the ^1H and ^{29}Si NMR spectra of **1** in argon-saturated d_6-benzene exhibit the expected resonances for a pseudo-C_2-symmetric molecule, and the ^{29}Si spectrum in d_8-toluene at −70 °C gave no evidence for a static agostic structure in solution on the NMR time scale. However, exposure of the sample to an atmospheric pressure of dinitrogen generated an additional set of 11 resonances in the ^1H spectrum and two new resonances in the ^{29}Si spectrum. Freeze−pump thawing (×3) of the sample led to complete disappearance of signals due to the new species **2**.[13] Green-black, X-ray-quality crystals of **2** were grown by fractional crystallization from a pentane solution of **1** under a 5 psi overpressure of N_2 at −20 °C, and the molecular structure is shown in Figure 2.[14]

2 has a binuclear structure, in which two units of **1** are bridged by a sideways-bound dinitrogen unit. The key structural feature of the latter is the N1−N2 bond length of 1.232(10) Å, consistent with an N−N double bond and comparable to that found in $[(TmCp^*)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (1.259(4) Å),[15] but significantly longer than the N−N triple bond in $[(U\{NN'_3\})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (1.109(7) Å).[2] It has been suggested that the inability of $[U(NN'_3)]$ to reduce N_2 is due to steric repulsion between the ligands in $[(U\{NN'\})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ and consequent poor orbital overlap between the uranium centers and the $\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$ fragment.[2] However, the U−N distances in **2** (2.401(8)−2.423(8) Å) are essentially identical (within esds) to those in $[(U\{NN'\})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$,[2] so the difference in N−N bond order is surprising, but may be a consequence of different frontier orbital geometries in the two ligand environments. The U_2N_2

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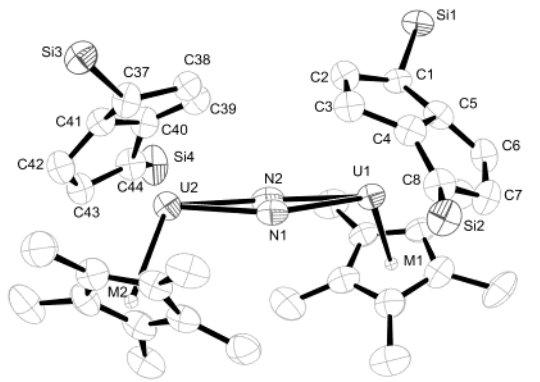
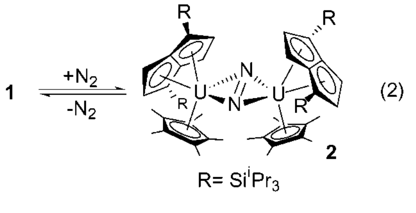


Figure 2. Molecular structure of **2** (isopropyl groups removed for clarity, thermal ellipsoids at 50%).

unit in the core of **2** is folded from planarity away from the pentalene ligands (presumably for steric reasons) by 5° about the N1−N2 bond, and relevant angles within the core are: 74.3(5)° (N2−N1−U1), 74.3(5)° (N2−N1−U2), 148.1(3)° (U1−N1−U2), 76.2(5)° (N1−N2−U1), 76.2(5)° (N1−N2−U2), and 151.9(3)° (U1−N2−U2). The two pentalene ligands are differentiated by slightly different fold angles (26° about C40−C41 and 22.5° about C4−C5), and the significant U-ring C interactions (to C37, C39, C42, C44, and to C1, C3, C6, C8), which range from 2.688(11) to 2.775(9), are essentially identical to those in **1**. Similarly, the U−Cp* centroid distances in **2** (U2−M2, 2.524 Å; U1−M1, 2.505 Å) are the same as that in **1** (2.486 Å) within esds. Hence the change in formal oxidation state from U(III) in **1** to U(IV) in **2** is not reflected in the structural parameters, but this is almost certainly due to the steric congestion in **2**.

Assuming that the low-temperature X-ray structure, in which the pentalene ligands are differentiated by different fold angles, is not maintained in solution, **2** has C_2 symmetry. The C_2 axis renders the two pentalene groups equivalent, but the two five-membered rings of the individual pentalene ligands are no longer symmetry-related, in agreement with the solution NMR data. The N═N stretch is predicted to be IR active in this point group; however, no absorptions assignable to this stretch were observed in the appropriate region of the IR spectrum in solution or the solid state for either **2-^{14}N** or **2-^{15}N**. This absorption may well be very weak, or obscured by the strong ligand vibrations in the region 1350−1500 cm^{-1}.

The reversible formation of **2** (eq 2) involves a formal oxidation of two U(III) centers to U(IV) with concomitant reduction of N_2 to N_2^{2-}.



However, even under 50 psi of N_2 the reaction only proceeds to ca. 75% completion in an NMR tube, and **2** loses dinitrogen extremely easily both in solution and the solid state.[16] The instability of **2** with respect to loss of N_2 and reformation of **1** is likely a reflection of the consequent relief of steric crowding and regeneration of the essentially parallel sandwich structure; this is in contrast to [U(NN′$_3$)], which is clearly pre-organized toward N_2 binding.

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Supporting Information Available: X-ray data for **1** and **2** (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Synthesis of **1** (under Ar). To a suspension of UI_3 (0.619 gm, 1 mmol) in Et_2O (75 mL) was added a suspension of KCp* (0.174 gm, 1 mmol) in Et_2O (25 mL) and the mixture stirred for 24 h. The resultant green solution was filtered from precipitated KI, stripped to dryness and final traces of Et_2O removed at 60 °C under vacuum. The residue was taken up in toluene (75 mL), and to this solution was added a solution of $K_2[C_8H_4\{Si^iPr_3\text{-}1,4\}_2]$ (0.492 g, 1 mmol) in toluene (25 mL) dropwise with stirring, and the mixture stirred for 6 h. The brown suspension was stripped to dryness, extracted with pentane (2 × 50 mL), and the pentane extracts were filtered through a pad of Celite on a frit. The resultant deep brown solution was concentrated to ca. 15 mL, and slow cooling to −45 °C afforded purple-black crystals of **1** which were isolated, washed with cold pentane (3 × 5 mL), and dried in vacuo. Yield 0.31 g, 40%. ^{1}H NMR (C_6D_6, 293 K): δ ppm −10.5 (br s, ^{i}Pr-C*H*$_3$, 18H), −13.4 (br s, ^{i}Pr-C*H*, 6H), −17.2 (br s, Cp*-C*H*$_3$, 15H), −20.1 (br s, pentalene ring-C*H*, 2H), −22.0 (br s, ^{i}Pr-C*H*$_3$, 18H), −42.2 (br s, pentalene ring-C*H*, 2H). ^{29}Si{^{1}H} NMR (C_6D_6, 298 K): δ ppm −176. ^{29}Si{^{1}H} NMR (C_7D_8, 201K): δ ppm −295. MS (EI): *m*/*z* 787 (M^+). Anal. Calcd for $C_{36}H_{61}Si_2U$: C, 54.87; H, 7.80. Found: C, 54.78; 8.29.
(9) Crystal data for **1**: Monoclinic, FW 788.06, in the space group $P2_1/n$ (No. 14); $a = 16.5194(4)$ Å, $b = 11.6816(3)$ Å, $c = 18.7404(5)$ Å, $\alpha = 90°$, $\beta = 90.504(1)°$, $\gamma = 90°$, $Z = 4$. Final residual wR2(all data) = 0.107 ($R = 0.062$, with goodness of fit 1.093 on F^2).
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(13) NMR data for **2** (C_6D_6, 293 K). ^{1}H: δ ppm 57.1 (br s, pentalene ring-C*H*, 1H), 53.4 (br s, pentalene ring-C*H*, 1H), 9.2 (br s, pentalene ring-C*H*, 1H), −2.4 (br s, ^{i}Pr-C*H*, 3H), −3.7 (br s, Cp*-C*H*$_3$, 15H), −3.75 (br s, ^{i}Pr-C*H*$_3$, 9H), −3.8 (br s, ^{i}Pr-C*H*$_3$, 9H), −4.1 (br s, ^{i}Pr-C*H*$_3$, 9H), −9.4 (br s, ^{i}Pr-C*H*$_3$, 9H), −12.4 (br s, pentalene ring-C*H*, 1H), −15.4 (br s, ^{i}Pr-C*H*, 3H). ^{29}Si{^{1}H}: δ ppm −108, −185.
(14) Crystal data for **2**: Monoclinic, FW 1604.14, in the space group $P2_1/n$ (No. 14); $a = 13.1165(3)$ Å, $b = 29.7960(5)$ Å, $c = 19.8885(10)$ Å, $\alpha = 90°$, $\beta = 109.203(8)°$, $\gamma = 90°$, $Z = 4$. Final residual wR2(all data) = 0.158 ($R = 0.071$, with goodness of fit 1.133 on F^2).
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