

Photochemically Promoted Bond-Cleavage and -Capture in a Diazomethane Derivative of a Triamidoamine Uranium(IV) Complex**

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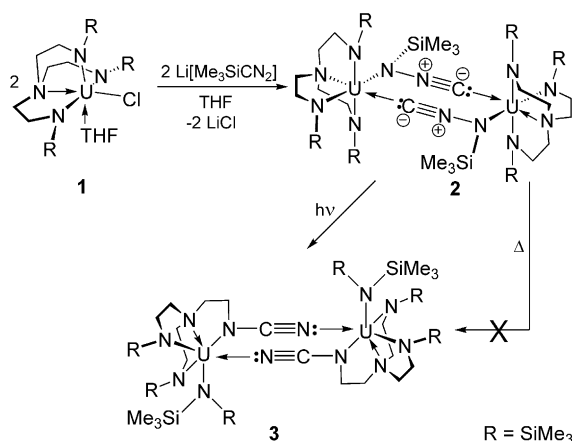
Compared to the wealth of photochemical studies of organo-metallic transition metal complexes,^[1] reports of organo-metallic actinide photochemistry are exceedingly rare.^[2] Apart from some early work by Marks et al. describing the formation of low-valent organometallic thorium and uranium complexes by photoinduced β -hydride elimination,^[3] nearly thirty years passed before Kiplinger et al. reported that photolysis of a uranium azide produces a transient uranium nitride.^[4] These notable but few contributions highlight the novel and essentially unexplored chemistry of actinide organometallics that may be accessed under photolytic conditions.

We have recently been investigating the chemistry of uranium complexes that are supported by triamido ligands, exemplified by $[\text{U}(\text{Cl})(\text{tren}^{\text{TMS}})(\text{THF})]$ (**1**, $\text{tren}^{\text{TMS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3$).^[5] More generally, uranium complexes supported by tripodal ligands have exhibited unique reactivities,^[6] and this, together with the dearth of organometallic uranium photochemical studies described above, prompted us to study the photochemistry of diazomethane derivatives of **1**. Diazomethanes have been extensively investigated in the d-block and have served as mimics for metal–dinitrogen binding,^[7] as carbene sources,^[8] and as reactive substrates.^[9] However, analogous f-block studies are few in number.^[10] For uranium, reactivity studies with diazoalkanes are scarce, and include oxidative addition to $\text{U}^{\text{III/IV}}$ to afford $\text{U}^{\text{V/VI}}=\text{N}=\text{N}=\text{CRR}'$ functionalities,^[11] insertion into a $\text{U}^{\text{IV}}-\text{Me}$ bond to give a hydrazonato derivative,^[12] and reaction with $[\text{U}^{\text{III}}\{\text{tacn}(\text{OAr})_3\}]$ to give a charge-separated radical anion or indazole following C–H activation.^[13] Together, these limited reports suggest novel f-block-diazoalkane reactivity trends that are distinct to the d-block.

Here, we report a photochemical investigation of uranium diazoalkane chemistry that reveals multiple bond cleavage that is not accessible thermally. All fragments are captured in a well-defined product,^[14] and this work highlights the novel bond activation chemistry that may be accessed in organo-

metallic uranium chemistry and this underscores the emerging complexity of f-block-diazoalkane reactivity.

Reaction of **1** with the salt obtained from lithiation of $\text{Me}_3\text{SiCHN}_2$ by $n\text{BuLi}$ afforded, after work-up, the isocyanotrimethylsilylamide complex $[\text{U}(\text{tren}^{\text{TMS}})\{\mu\text{-N}(\text{SiMe}_3)\text{NC}\}]_2$ (**2**) as green blocks in 52 % crystalline yield (Scheme 1). The FTIR spectrum of **2** exhibits only one absorption in the CN multiple bond region at 2122 cm^{-1} . The ^1H NMR spectrum exhibits nine resonances spanning the range $\pm 69\text{ ppm}$, consistent with a pseudo mirror plane symmetry at uranium on the NMR timescale, and although two tren *N*-silyl groups are equivalent, the methylene protons resonate as six broad singlets. Variable-temperature NMR studies did not provide evidence for any dynamic processes. Together, these observations suggest that only the diazomethane *N*-silyl isomer is isolated (see below).^[10c]



Scheme 1. Synthesis of **2** and **3**.

A crystallographic study of **2** (Figure 1)^[15] revealed a centro-symmetric dimer. Refining silyl-disorder models led to the *N*-silyl isomer exclusively. The N(5)–Si(4) bond length of $1.763(2)\text{ \AA}$ compares well to the tren N–Si distances [$1.725(2)$ – $1.732(2)\text{ \AA}$] and not to typical C–Si bond lengths (1.81 – $1.84\text{ \AA}$).^[16] The U(1)–N(5) bond [$2.586(2)\text{ \AA}$] is longer than the U–N_{amide} bonds [$2.232(2)$ – $2.267(2)\text{ \AA}$] and the N(5)–N(6) bond is short [$1.308(3)\text{ \AA}$]. This suggests that both the $\text{U} \leftarrow \text{N}(\text{SiMe}_3)=\text{N}^+=\text{C}^--\text{U}$ and $\text{U}-\text{N}(\text{SiMe}_3)-\text{N}^+=\text{C}^--\text{U}$ resonance forms contribute to **2**, although the N(6)–C(19) bond is short [$1.176(3)\text{ \AA}$]. The U(1)–C(19) bond length of $2.540(2)\text{ \AA}$ compares to $\text{UC}\equiv\text{N}$ distances of $2.59(2)$ and

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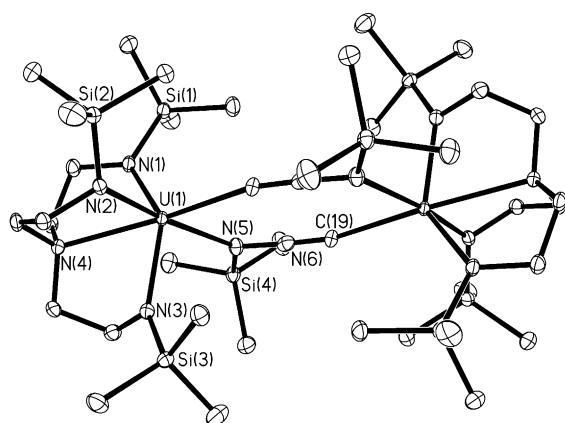


Figure 1. Molecular structure of **2** with selected labeling and displacement ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: U(1)–N(1) 2.260(2), U(1)–N(2) 2.267(2), U(1)–N(3) 2.232(2), U(1)–N(4) 2.655(2), U(1)–N(5) 2.586(2), U(1)–C(19A) 2.540(2), N(5)–N(6) 1.308(3), N(6)–C(19) 1.176(3), N(1)–Si(1) 1.732(2), N(2)–Si(2) 1.726(2), N(3)–Si(3) 1.725(2), N(5)–Si(4) 1.763(2).

2.415(6) Å in $[\text{U}(\eta^5\text{-C}_5\text{H}_5)_3(\text{OTf})(\text{CNrBu})]^{[17]}$ and $[\text{U}(\eta^5\text{-C}_5\text{H}_7\text{Bu}_3)_2(\text{OSiMe}_3)(\text{CN})]^{[18]}$ respectively.

The UV/Vis spectrum of **2**^[19] is dominated by a broad charge-transfer band which tails in to 450 nm from the UV region. Additionally, weak transitions were observed in the range 520–950 nm ($\epsilon = 10\text{--}20\text{ M}^{-1}\text{ cm}^{-1}$) which are characteristic of Laporte-forbidden $f \rightarrow f$ transitions for uranium(IV).^[20] Mindful of Jørgensen's considerations of empirical optical electronegativity^[21] we selected a 125 W medium pressure mercury lamp to study the photochemistry of **2**.^[22] We found that photolysis of a toluene solution of **2** at room temperature for 4 h resulted in quantitative, and clean, conversion to a new product as revealed by ¹H NMR spectroscopy. In contrast, the thermolysis of **2** at 110 °C for 3 days gave no reaction. Heating **2** to higher temperatures eventually resulted in annihilation of **2** and the formation of intractable products.

Following photolysis and work-up, green tablets of $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2(\mu\text{-CH}_2\text{CH}_2\text{NC}\equiv\text{N})\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (**3**) were isolated in which extensive bond-cleavage, -formation, and reorganization has occurred (Scheme 1). The FTIR spectrum of **3** exhibits one strong absorption in the CN multiple bond region at 2152 cm^{-1} , which is hypsochromically shifted by 30 cm^{-1} compared to **2**, and this is commensurate with the presence of a cyano group in **3** compared to the isocyano group in **2**. The ¹H NMR spectrum of **3** exhibits six resonances in the range +51 to –42 ppm, which is consistent with two equivalent tren *N*-silyl groups resulting from a pseudo mirror plane symmetry at uranium on the NMR timescale and the formation of a $\text{N}(\text{SiMe}_3)_2$ amide group.

The molecular structure of **3** was confirmed by crystallography and was shown to be a centrosymmetric dimer constructed via bridging cyano groups (Figure 2).^[15] The U(1)–N(3) bond of 2.505(7) Å is longer than the two “normal” U(1)–N(1) and U(1)–N(2) bonds of 2.255(7) and 2.224(7) Å, respectively. Additionally, the N(3)–C(11) [1.281(12) Å] and C(11)–N(4) [1.173(12) Å] bonds are short, and the U(1)–N(4A) bond of 2.484(8) Å is shorter

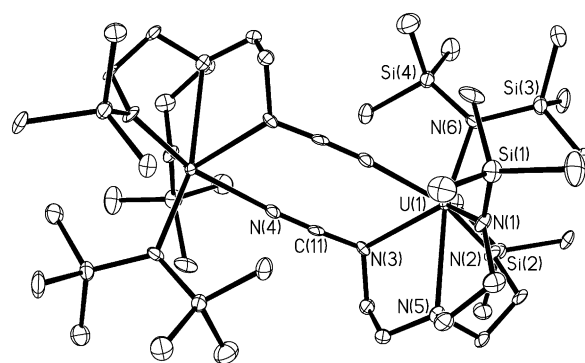


Figure 2. Molecular structure of **3** with selected labeling and displacement ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: U(1)–N(1) 2.255(7), U(1)–N(2) 2.224(7), U(1)–N(3) 2.505(7), U(1)–N(4A) 2.484(8), U(1)–N(5) 2.744(7), U(1)–N(6) 2.331(7), N(3)–C(11) 1.281(12), C(11)–N(4) 1.173(12), N(1)–Si(1) 1.742(72), N(2)–Si(2) 1.734(7), N(6)–Si(3) 1.733(7), N(6)–Si(4) 1.718(8).

than the U(1)–N(3) bond. Taken together, this indicates that both the $\text{U} \leftarrow \text{N}\equiv\text{C}-(\text{RCH}_2)\text{N}-\text{U}$ and $\text{U}-\text{N}=\text{C}=(\text{RCH}_2)\text{N} \rightarrow \text{U}$ resonance forms contribute to **3**.

Studies have shown several isomers of the lithium salt are possible (Figure 3)^[23] and a *C*–*N*–*SiMe*₃ isomer equilibrium has been reported for Me_3SiCN_2 when coordinated to germanium.^[24] Assuming $\text{Li}[\text{Me}_3\text{SiCN}_2]^{[10c]}$ has a *C*-silyl group then a 1,3-silyl-shift from carbon to nitrogen is required during the formation of **2**. In the reaction to produce **3**, *N*–*Si*, and *N*–*N* bonds have been cleaved, at the very least, and one *C*–*N* bond and *N*–*Si* bond have been formed. This contrasts to previous work^[4] in which *N*–*Si* bonds remained apparently unchanged after photolysis.^[25] Overall, it appears that the distal nitrogen of the diazomethane is functionalized with two silyl groups, and the distal-proximal *N*–*N* bond is cleaved to formally release a “ NC^+ ” fragment which is captured by the “ RN^{2-} ” arm of the tren ligand. Of course, uranium(III) is an accessible oxidation state so homolytic bond scission could be postulated.^[3] Since the UV/Vis spectrum of **3** is distinct to that of **2**,^[19] we monitored the photolysis of **2** with the exclusion of sub-300 nm radiation. Under these conditions we noted that **3** was not formed, which suggests that neither the *f*-manifold nor the metal–ligand linkages are involved in the promotion of this reaction.^[21] However, this does not rule out their subsequent involvement, but it seems that intra-ligand excitations promote this reaction. Monitoring the unfiltered reaction by NMR and FTIR spectroscopy shows only the growth of resonances/absorptions attributable to **3** with

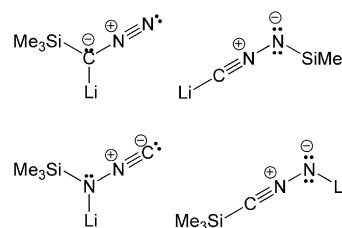


Figure 3. Possible monomeric isomers of $\text{Li}[\text{Me}_3\text{SiCN}_2]$.

concomitant reduction in peak intensities associated with **2**. Also, reacting **1** with $\text{Li}[\text{Me}_3\text{SiCN}_2]$ under photolytic conditions straightforwardly affords **3**. As far as we are aware, the transformation of **2** to **3** has no precedent in diazoalkane chemistry^[7–9] and contrasts to typical organometallic d-block photochemical reactions.^[1,26,27]

To summarize, we have reported a facile photochemically promoted reaction which involves multiple bond-cleavage and -capture to give a well-defined product. The transformation of **2** to **3** is not thermally accessible and has no precedent in diazoalkane chemistry. This work highlights the novel bond activation chemistry that may be accessed in organometallic uranium chemistry, and it underscores the emerging complexity of f-block-diazoalkane reactivity. We are examining the photochemistry of other related complexes to address the paucity of data in the area.

Experimental Section

Synthesis of 2: THF (15 mL) was added to a cold (-78°C) mixture of **1** (0.71 g, 1.00 mmol) and $\text{Me}_3\text{SiC}(\text{Li})\text{N}_2$ (0.12 g, 1.00 mmol). The resulting green solution was allowed to warm to ambient temperature and stirred for 16 h. Volatiles were removed in vacuo to yield a green sticky solid. Toluene (10 mL) was added. The resulting green-brown suspension was warmed to ca. 60°C and allowed to cool and settle (1 h). Following filtration from the white solid and removal of volatiles in vacuo, the green-brown residue was dissolved in hot C_6H_6 (70°C , 15 mL) and stored at 8°C for 24 h to afford green X-ray quality crystals of **2**. A second crop was obtained by reducing the volume of C_6H_6 to ca. 5 mL and storage at 8°C for 24 h. Yield: 0.37 g (52%). Anal. calcd for $\text{C}_{38}\text{H}_{96}\text{N}_{12}\text{Si}_8\text{U}_2$ (%): C 32.10, H 6.81, N 11.83; found: C 31.93, H 6.78, N 11.89. ^1H NMR: (C_6D_6 , 298 K): $\delta = -68.22$ (s, 2H, CH_2), -43.95 (s, 2H, CH_2), -29.96 (s, 2H, CH_2), -15.06 (s, 18H, SiMe_3), -6.65 (s, 2H, CH_2), 11.46 (s, 9H, SiMe_3), 12.77 (s, 2H, CH_2), 20.23 (s, 9H, $[\text{N}(\text{SiMe}_3)\text{NC}]$), 68.88 ppm (s, 2H, CH_2). μ_{eff} (Evans method, C_6D_6 , 298 K): $3.15 \mu_{\text{B}}$. FTIR (Nujol): $\tilde{\nu} = 2726.97$ (w), 2672.93 (w), 2360.28 (w), 2342.73 (w), 2121.85 (vs), 1958.81 (w), 1604.14 (m), 1549.28 (m), 1305.20 (m), 1259.83 (s), 1094.06 (m), 1079.14 (s), 1052.95 (s), 1020.17 (s), 982.06 (s), 928.72 (m), 876.11 (m), 839.66 (s), 801.57 (s), 770.45 (m), 740.06 (m), 722.20 (m), 861.76 (w), 632.27 (w), 615.76 (w), 600.19 (w), 546.39 (w), 465.03 (m), 438.18 cm^{-1} (m).

Synthesis of 3: A solution of **2** (200 mg, 0.14 mmol) in toluene (15 mL) was irradiated with 125 W UV-lamp at ambient temperature for 4 h. The solvent was removed in vacuo to yield a sticky brown solid. The yield was found to be quantitative by NMR spectroscopy. Dissolution of the brown solid in hot C_6H_6 (70°C , 2 mL) and storage at 8°C for 24 h afforded green, X-ray quality crystals of **3**. Anal. calcd for $\text{C}_{38}\text{H}_{96}\text{N}_{12}\text{Si}_8\text{U}_2$ (%): C 32.10, H 6.81, N 11.83; found: C 32.49, H 6.82, N 11.82. ^1H NMR: (C_6D_6 , 298 K): $\delta = -41.85$ (s, 1H, CH_2), -40.27 (s, 1H, CH_2), -39.72 (s, 1H, CH_2), -38.74 (s, 1H, CH_2), -27.74 (s, 9H, $[\text{N}(\text{SiMe}_3)_2]$), -27.24 (s, 9H, $[\text{N}(\text{SiMe}_3)_2]$), -24.45 (s, 1H, CH_2), -23.10 (s, 1H, CH_2), -22.94 (s, 1H, CH_2), -11.50 (s, 1H, CH_2), -12.30 (s, 9H, SiMe_3), 5.72 (s, 1H, CH_2), 8.38 (s, 1H, CH_2), 11.45 (s, 1H, CH_2), 40.19 (s, 1H, CH_2), 50.76 ppm (s, 9H, SiMe_3). μ_{eff} (Evans method, C_6D_6 , 298 K): $3.74 \mu_{\text{B}}$. FTIR (Nujol): $\tilde{\nu} = 2727.63$ (w), 2673.57 (w), 2289.29 (w), 2151.66 (vs), 1959.00 (w), 1590.22 (w), 1298.29 (w), 1258.73 (m), 1248.70 (m), 1202.04 (w), 1146.23 (w), 1078.26 (m), 1054.17 (m), 1020.80 (m), 928.53 (s), 901.96 (m), 842.06 (s), 772.07 (m), 717.08 (m), 675.65 (m), 632.59 (m), 610.32 (w), 579.70 (w), 568.08 (w), 554.45 (w), 554.45 (w), 546.98 (w), 523.67 (w), 437.27 cm^{-1} (m).

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