

Ligand Metalation in the Reactivity of a Tetravalent Uranium Amides

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The reactions of organolithium reagents with the tetravalent $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ and its DME solvate have been examined. Treatment of both compounds with methyl-lithium in diethyl ether resulted in one electron reduction of the metal center and γ -deprotonation of one of the ligands. The dimeric $\{\text{U}[(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)]_2[\mu\text{-Li}(\text{DME})]\}_2$ (**1**) was isolated from the reaction mixture regardless of the amount of MeLi employed. The employment of $\text{LiCH}_2\text{SiMe}_3$ in DME led instead to multiple γ -deprotonation events at the same carbon atom with formation of the trimetallic $\{\text{U}[(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)]_2[\text{U}[(\mu^3\text{-C-SiMe}_2)\text{N}(\text{SiMe}_3)]_2]\}_2\{\mu\text{-OMe}\}$ (**2**) cluster centered on a fully deprotonated carbon atom. Crystallographic analysis revealed the presence of $\mu\text{-OCH}_3$ units in the cluster as generated by DME solvent cleavage. A similar reaction carried out in the absence of DME led to the isolation of a closely related trimetallic $\{\text{U}[(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)]_2[\text{U}[(\mu^3\text{-C-SiMe}_2)\text{N}(\text{SiMe}_3)]_2]\}_2\{\mu\text{-CH}_2\text{-SiMe}_2\text{-N}(\text{SiMe}_3)\}$ (**3**). One additional γ -deprotonated fragment replacing the bridging methoxy group of **2** was present in this case. The presence of a fully deprotonated carbon atom bridging three metal centers and of one silicon atom was confirmed by both X-ray structures and NMR data. An attempt to reduce $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ with KC_8 in a coordinating solvent resulted in ligand scrambling with the formation of two products. The first is a trimeric U(III) cluster formulated as $\{\text{U-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2][\text{DME}]\}_3\{\text{U-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2]_2\}\{\mu_3\text{-Cl}\}_2$ (**4**). The second was $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$. A similar reduction reaction carried out in noncoordinating toluene resulted instead in an attack on the ligand affording the dimeric $\{\text{U-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)]\}_2$ (**5**). Alkylation of $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ with *n*-butyl-lithium in hexane surprisingly yielded the pentavalent $\text{U}[(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)]_2[\text{N}(\text{SiMe}_3)_2]$ (**6**). The acquisition of one additional ligand during the reaction hinted at the presence of other products in the reaction mixture.

Introduction

It is today commonly agreed that low valent uranium has the potential for providing a rich and diversified chemical reactivity of the caliber of that observed for some divalent lanthanides. Among the most exciting and promising

transformations reported so far in the literature are dinitrogen activation/reduction¹ and cleavage,² depolymerization of poly silanols with cleavage of the Si–O bond,² CO oligomerization,³ unusual coordination of small molecules,⁴ including a unique case of $\text{sp}^3\text{-C-H}$ bond coordination,^{4a} and oxidative elimination of H_2 .⁵

As usual, ligand features are central to the performance of the metal and to the stabilization of the low-oxidation state. First, it should be noticed that authentic oxidation states lower than +3 are unknown for uranium. Only in the presence of π -systems have a few reduced species (or low-valent synthons) been prepared and characterized.^{6–8} The particular nature of the ligand donor atom also seems to be of primary importance. The reactivity of low-valent uranium becomes particularly enhanced in the presence of nitrogen donor atoms as indicated by the few cases of dinitrogen reversible fixation¹ and cleavage.² The first well-documented reduction affording a highly reduced uranium complex with

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an "inverted-sandwich" structure was obtained by using bulky amido ligands.^{6,7} Furthermore, bulky amido ligands may be effectively used also for the purpose of obtaining solvent-free compounds given that the presence of solvent in the coordination sphere often leads to fragmentation processes interfering with the reactivity of the metal center.⁹

This background prompted us to revisit the reduction chemistry of uranium supported by the *bis*-silazane anion. This ligand has been successfully used by Andersen et al. in his pioneering work in the chemistry of the tetravalent state.¹⁰ In the field of f-block element chemistry, it is known to afford low coordinate complexes with excellent yields for several metals.¹¹ Low coordination numbers, the absence of coordi-

nated solvent molecules, and high solubility in hydrocarbons and aromatic solvents in addition to high ligand basicity, altogether, make these derivatives excellent precursors for reactivity studies.^{1d,7b,11,12} A recurrent feature discovered so far for this ligand system is its direct involvement in the organometallics chemistry of the metal center (γ -metalation). In the chemistry of uranium, products resulting from γ -metalation were utilized for a variety of organometallic transformations including nucleophilic behavior¹³ and insertion reactions¹⁴ and for discovering examples of unusual reactivity.^{14a,c} Furthermore, the lability of the Si–N bond, in combination with the availability of electrons provided by the reduced state, allows formation of bridging or terminally bonded imido groups^{6b,13a,14b,15} via elimination of one of the two Me₃Si residues.¹⁶ As far as the trivalent state is concerned, U[N(SiMe₃)₂]₃ is known but does not display unusual reactivity. This behavior is certainly not typical for a U(III) metal center which, when combined to N-donor atoms, characteristically shows extreme reactivity.^{1b,c,3,4,17} On the other hand, the large bulk generated by the three equatorial ligands makes the metal inaccessible to reagents other than protons.

In this work, we have studied the reduction chemistry of tetravalent uranium silazane derivatives aiming at exploring the possibility of preparing lower-valent complexes for reactivity purposes. As correctly observed by Andersen et al., we also observed that this chemistry is indeed dominated by γ -metalation. Herein, we report how different extents of γ -deprotonation may lead to cluster formation. It was also observed that attempts to lower the oxidation state with strong reductants resulted instead in reoxidation of the metal center at the expense of the ligand possibly through disproportionative pathways.

Experimental Section

All operations were performed under a nitrogen atmosphere with rigorous exclusion of oxygen and water using standard Schlenk and glovebox techniques. Hexane and toluene solvents were purified by passing through Al₂O₃ filled columns and deoxygenated prior to use by several vacuum/nitrogen purges. DME was dried over LiAlH₄ and distilled under N₂ prior to utilization. Benzene-d₆ was obtained from "C/D/N isotopes", dried over Na/K alloy, distilled, and stored over molecular sieves (4A). *n*-Butyl-lithium solution (2.5 M) in hexane and methyl-lithium solution (1.6 M) in diethyl ether were purchased from Aldrich and used as received. LiCH₂(SiMe₃) was prepared according to a modified literature procedure¹⁸ using boiling cyclohexane as a solvent.

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KC₈ was prepared according to a literature procedure.¹⁹ Complexes {UCl₂[N(SiMe₃)₂]₂}₂ and UCl₂[N(SiMe₃)₂]₂[C₄H₁₀O₂] were synthesized according to literature procedures.²⁰ Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods, and corrections for underlying diamagnetism were applied to the data.²¹ NMR spectra were recorded at 293 K on a Varian Inova 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and reported in parts per million relatively to Me₄Si. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Bruker diffractometer equipped with a 1K SMART CCD area detector. Chemical degradation experiments were performed in a sealed vessel connected to a high vacuum line, by condensing a stoichiometric amount of gaseous HCl over the sample kept at liquid N₂ temperatures. After reaching room temperature, the volatiles were pumped off and collected with a Toepler pump and analyzed using a GC with a molecular sieves column and TC detector.

Preparation of {U[(μ-CH₂-SiMe₂)N(SiMe₃)₂][μ-Li(DME)]₂} (1). A solution of methyl-lithium (9 mL of 1.6 M, 14.4 mmol) in diethyl ether was slowly added to a cooled solution (−37 °C) of UCl₂[N(SiMe₃)₂]₂(DME) (3.40 g, 4.72 mmol) in DME (20 mL). The reaction mixture was allowed to warm up to room temperature under vigorous stirring. The color changed from the initial pale-green to intense brown-red while a colorless insoluble material separated. After 2 additional hours of stirring at room temperature, the solvent was removed *in vacuo* and the resulting orange solid suspended in hexane (35 mL). The insoluble materials were eliminated by centrifugation and the volume reduced (11 mL) by evaporation *in vacuo*. The solution was allowed to stand at −37 °C for 48 h, after which dark red-orange prisms were formed. After washing with cold hexane (−37 °C, 3 mL) and drying for 30 min under N₂, crystalline **1** was obtained (2.87 g, 4.12 mmol, 87%). Upon further drying, dark red-orange crystals of **1** deteriorated with the formation of yellow-orange powdery material. Elem Anal. for UC₁₆H₄₄LiN₂O₂Si₄ found (calculated): C, 29.31 (29.39); H, 6.63 (6.78); N, 4.23 (4.28). ¹H NMR (500 MHz, benzene-d₆, 20 °C): δ 3.30 (6H, DME, CH₃-O), 3.12 (4H, DME, -CH₂-O), -13.10 (12H, Si-(CH₃)₂), -28.57 (18H, Si-(CH₃)₃), -47.02 (4H, Si-CH₂-U). IR (Nujol, KBr, cm⁻¹): 1602 (sh), 1482 (sh), 1453 (s), 1246 (m), 980 (vs), 822 (vs), 675 (w), 632 (m), 614 (m), 479 (m), 434 (w). μ_{eff} = 2.53 μ_B.

Preparation of {U[(μ-CH₂-SiMe₂)N(SiMe₃)₂][N(SiMe₃)₂]₂-{U[(μ³-C-SiMe₂)N(SiMe₃)₂][N(SiMe₃)₂]} (μ-OMe)} (2). A solution of UCl₂[N(SiMe₃)₂]₂(DME) (0.764 g, 1.0 mmol) in hexane (10 mL) was combined with a solution of LiCH₂SiMe₃ (0.20 g, 2.2 mmol) in the same solvent (5 mL). An instant color change from pale green to dark orange, accompanied by the formation of pale insoluble material, was observed upon mixing. Stirring was continued at room temperature for an additional 2 h, and the insoluble material was eliminated by centrifugation. The resulting solution was concentrated to about 5 mL and allowed to stand at −37 °C. After three days, dark orange crystals were formed, which were separated, washed with cold hexane (3 mL, −37 °C), and dried under a N₂ atmosphere (0.44 g, 0.26 mmol,

74%). Elem. Anal. for U₃C₃₇H₁₀₆N₆O₂Si₁₂ found (calculated): C, 25.97 (26.10); H, 6.14 (6.28); N, 4.90 (4.94). ¹H NMR (500 MHz, benzene-d₆, 20 °C): δ 29.36 (27H, N-Si(CH₃)₃), 9.85 (3H, O-CH₃), 7.19 (54H, N[Si-(CH₃)₃]₂), -0.13 (broad, 18H, Si-(CH₃)₂), -46.90 (4H, Si-CH₂-U). IR (Nujol mull, cm⁻¹): 1589 (sh), 1261 (s), 1162 (s), 968 (vs), 926 (vs), 850 (vs), 769 (s), 710 (m), 670 (m), 639 (w), 561 (sh), 476 (sh), 443 (m), 415 (m). μ_{eff} = 1.79 μ_B.

Preparation of {U[(μ-CH₂-SiMe₂)N(SiMe₃)₂][N(SiMe₃)₂]₂-{U[(μ³-C-SiMe₂)N(SiMe₃)₂][N(SiMe₃)₂]} (μ-CH₂-SiMe₂)N(SiMe₃)₂} (3). A suspension of UCl₂[N(SiMe₃)₂]₂ (0.45 g, 0.7 mmol) in hexane (20 mL) was combined with a solution of LiCH₂SiMe₃ (0.14 g, 1.5 mmol) in the same solvent (5 mL). An instant color change from pale green to dark brown was observed upon addition. After 6 h of stirring at room temperature, the solvent was removed *in vacuo*. The resulting dark-brown powdery material was extracted with hexane (30 mL). The volume of the extract was reduced to 7 mL and the solution allowed to stand at −37 °C for 4 days. Dark brown prisms of **3** were formed, which were separated, washed with cold hexane (5 mL, −37 °C), and dried under a N₂ atmosphere (0.26 g, 0.16 mmol, 67%). Elem. Anal. for U₃C₃₆H₁₀₂N₆Si₁₂ found (calculated): C, 25.57 (25.89); H, 6.07 (6.16); N, 4.99 (5.03). ¹H NMR (500 MHz, benzene-d₆, 20 °C): δ 24.11 (36H, N-Si(CH₃)₃), 7.22 (36H, N[Si-(CH₃)₃]₂), -13.48 (18H, Si-(CH₃)₂), -16.85 (6H, Si-(CH₃)₂), -43.10 (6H, Si-CH₂-U). IR (Nujol mull, cm⁻¹): 1627 (sh), 1259 (vs), 1093 (vs), 1022 (vs), 800 (br, vs). μ_{eff} = 1.65 μ_B.

Preparation of {U-μ-Cl[N(SiMe₃)₂][DME)]₂{U-μ-Cl[N(SiMe₃)₂]₂} (μ³-Cl)} (4). A solution of UCl₂[N(SiMe₃)₂]₂(DME) (1.60 g, 2.2 mmol) in DME (25 mL) was treated with freshly prepared KC₈ (0.61 g, 4.5 mmol). The mixture was stirred at room temperature for 3 days, during which the color slowly changed to dark red-purple. When no further color change could be detected, the solvent was removed *in vacuo* and the residual dark-red solid was extracted with boiling toluene (15 mL). The volume of the dark-red solution was reduced to 5 mL and allowed to stand at room temperature for 48 h. Two different crystalline materials (dark-red blocks and purple needles) separated in the mixture. After washing with hexanes (40 mL) at room temperature, the needle-shaped crystals completely disappeared. Recrystallization of the remaining solid material from hot toluene led to the isolation of dark-red blocks of **4** (0.69 g, 0.4 mmol, 52%). Elem. Anal. for U₃C₃₉H₁₀₀C₁₅N₄O₄Si₈ found (calculated): C, 25.87 (25.95); H, 5.47 (5.58); N, 3.09 (3.10). IR (Nujol mull, cm⁻¹): 1604 (sh), 1459 (s), 1444 (vs), 1247 (br vs), 1086 (m), 1014 (m), 908 (vs), 879 (sp), 840 (vs, b), 782 (s), 758 (s), 694 (vs), 669 (vb). The hexanes extracted were concentrated (10 mL) and allowed to stand at −37 °C, affording crystals of the second compound. A database search of the crystallographic cell parameters identified this second product as U[N(SiMe₃)₂]₃.²² μ_{eff} = 1.47 μ_B.

Preparation of {U-μ-Cl[N(SiMe₃)₂]₂[N(SiMe₃)₂]} (5). A suspension of UCl₂[N(SiMe₃)₂]₂ (0.26 g, 0.4 mmol) in 20 mL of toluene was treated with freshly prepared KC₈ (0.17 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 7 days, during which, the color steadily changed from pale green to deep brown-red. The solvent was then removed *in vacuo* and the residual dark brown-red solid extracted with hexanes (35 mL). The volume of hexane extracts was reduced *in vacuo* to 10 mL and allowed to stand at −37 °C. After 3 days, a mixture of crystals with two different shapes was obtained. Fractional crystallization from toluene/hexane mixtures afforded dark brown-red prisms of **5** (0.12 g, 0.1 mmol, 42%). Storage of the mother liquor at −37 °C for 3 additional days afforded complex **6** in crystalline form (0.05 g, 0.04 mmol, 18%). Elem. Anal. for

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$\text{U}_2\text{C}_{30}\text{H}_{90}\text{Cl}_2\text{N}_6\text{Si}_{10}$ found (calculated): C, 26.40 (26.44); H, 6.47 (6.66); N, 6.15 (6.17). IR (Nujol mull, cm^{-1}): 1578 (sh), 1259 (e), 1160 (e), 973 (vs), 919 (vs), 843 (vs), 777 (s), 715 (m), 675 (m), 644 (w), 556 (sh), 470 (sh), 440 (m), 415 (m). $\mu_{\text{eff}} = 2.48 \mu_{\text{B}}$.

Preparation of $\text{U}[(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)]_2[\text{N}(\text{SiMe}_3)_2]$ (6**).** A suspension of $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ (0.500 g, 0.79 mmol) in cold hexane (-37°C , 15 mL) was treated with a cooled solution of *n*-BuLi in the same solvent (0.65 mL, 2.5 M, 1.63 mmol). The reaction mixture was allowed to warm to room temperature while being vigorously stirred. The color of the solution changed to dark purple-red and a visible amount of insoluble material appeared. After stirring for 4 h at room temperature, the solvent was removed *in vacuo* and the resulting solid residue extracted with 30 mL of boiling hexane. The volume of the extract was reduced to 10 mL, and the solution was allowed to be left standing at -37°C . Dark-red prisms of **6** were formed in 3 days, which were washed with cold hexanes (3 mL) and dried under a N_2 atmosphere (0.183 g, 0.26 mmol, 33%). Elem. Anal. for $\text{UC}_{18}\text{H}_{52}\text{N}_3\text{Si}_6$ found (calculated): C, 30.07 (30.15); H, 7.17 (7.31); N, 5.79 (5.86). IR (Nujol mull, cm^{-1}): 1585 (sh), 1249 (s), 1152 (s), 960 (vs), 930 (vs), 845 (vs), 759 (s), 722 (m), 676 (m), 631 (w), 551 (sh), 444 (w), 425 (w). $\mu_{\text{eff}} = 1.48 \mu_{\text{B}}$.

X-Ray Crystallography

For all the compounds, the results presented are the best of several trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Crystals in general scattered very poorly and displayed an additional tendency to rapidly decay under the X-ray beam. Therefore, data collection times have been necessarily short. In turn, this resulted in poor scattering at a wide angle and occasionally in poor crystal solution parameters. Nonetheless, in every case, the quality of the structures was sufficient to establish the connectivity. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer. Data for all the compounds were collected with a sequence of $0.3^\circ \omega$ scans at 0, 120, and 240° in φ . Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.²³ Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic $P2_1/n$ for **1** and **5**; triclinic $P\bar{1}$ for **2**, **3**, and **4**; and orthorhombic $Pnma$ for **6**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 . In all the structures, the compound molecules were located in general positions. The structures of complexes **1** and **5** represent dimeric formations with two monomeric units related by an inversion center symmetry operator. The structure of complex **6** displays a 50:50 disorder of the U moiety with two disordered units related by a mirror plane symmetry operator. Carbon atoms of a cocrystallized hexane solvent molecule in **1** were refined isotropically due to partial occupancy coupled with significant thermal motion disorder and in order to maintain an optimal data to parameters ratio. In all the structures, all non-hydrogen atoms, with the exceptions mentioned above, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All

Table 1. Crystal Data and Data Collection Parameters of Complexes **1**, **2**, and **3**

	1	2	3
formula	$\text{U}_2\text{C}_{38}\text{H}_{102}\text{-Li}_3\text{N}_4\text{O}_4\text{Si}_8$	$\text{U}_3\text{C}_{37}\text{H}_{106}\text{-N}_6\text{OSi}_{12}$	$\text{U}_3\text{C}_{36}\text{H}_{102}\text{-N}_6\text{Si}_{12}$
fw	1393.90	1702.45	1670.41
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	14.862(3)	11.923(3)	14.826(3)
<i>b</i> , Å	11.980(2)	13.947(4)	15.141(3)
<i>c</i> , Å	18.250(3)	22.855(6)	15.561(3)
α , deg	90	79.887(6)	75.030(3)
β , deg	97.579(4)	75.655(5)	89.431(4)
γ , deg	90	67.832(5)	86.129(4)
volume, Å ³	3220.8(10)	3395.7(15)	3366.8(12)
<i>Z</i>	2	2	2
ρ_{calc} g/cm ³	1.437	1.665	1.648
μ , mm ⁻¹	5.203	7.378	7.438
<i>F</i> (000)	1384	1644	1608
<i>T</i> range (deg)	1.66–20.81	1.58–21.96	1.35–28.50
limiting indices	$\pm 14, 0$ to $+11, 0$ to $+18$	$\pm 12, \pm 14, 0$ to $+23$	$\pm 19, \pm 19, 0$ to $+20$
(<i>h, k, l</i>) reflns collected/unique	3309/3309	8068/8068	23433/14059
<i>R</i> _{int}	0.0000	0.0000	0.0218
GOF	0.647	0.934	1.013
<i>R</i> 1 (obs/all)	0.0476/0.0868	0.0668/0.1664	0.0285/0.0399
w <i>R</i> 2 (obs/all)	0.0897/0.0961	0.0797/0.0985	0.0659/0.0706

	4	5	6
formula	$\text{U}_3\text{C}_{39}\text{H}_{100}\text{-Cl}_5\text{N}_4\text{O}_4\text{Si}_8$	$\text{U}_2\text{C}_{30}\text{H}_{90}\text{-Cl}_2\text{N}_6\text{Si}_{10}$	$\text{UC}_{18}\text{H}_{52}\text{-N}_3\text{Si}_6$
fw	1805.29	1362.94	717.20
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$Pnma$
<i>a</i> , Å	15.1810(17)	11.910(3)	18.607(3)
<i>b</i> , Å	15.6704(18)	14.303(3)	8.440(1)
<i>c</i> , Å	15.9987(18)	17.715(4)	21.682(3)
α , deg	78.675(2)	90	90
β , deg	87.335(2)	99.568(3)	90
γ , deg	66.676(2)	90	90
volume, Å ³	3424.8(7)	2975.8(11)	3405.2(8)
<i>Z</i>	2	2	4
ρ_{calc} g/cm ³	1.751	1.521	1.399
μ , mm ⁻¹	7.445	5.751	4.988
<i>F</i> (000)	1734	1340	1428
<i>T</i> range (deg)	1.75–21.96	1.84–28.90	2.17–21.96
limiting indices	$\pm 16, \pm 17, 0$ to $+17$	$\pm 13, \pm 18, \pm 22$	$\pm 19, \pm 8, \pm 22$
(<i>h, k, l</i>) reflns collected/unique	30603/9777	16720/6814	23771/2383
<i>R</i> _{int}	0.2162	0.0597	0.0939
GOF	1.034	1.053	1.031
<i>R</i> 1 (obs/all)	0.0631/0.1145	0.0475/0.0959	0.0448/0.0844
w <i>R</i> 2 (obs/all)	0.1354/0.1467	0.0797/0.0907	0.0752/0.0848

scattering factors are contained in several versions of the SHELXTL program library, version 6.12.²⁴ Crystallographic data for all structures are reported in Table 1. Selected bond distances and angles are given in the Supporting Information.

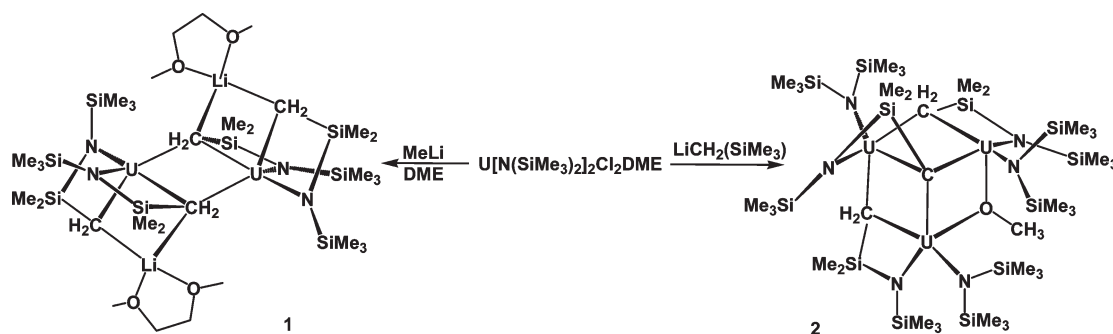
Results and Discussion

As previously observed by Andersen et al.,¹⁰ attempts to alkylate the tetravalent uranium *tris*-amido-chloride complex $\text{UCl}[\text{N}(\text{SiMe}_3)_2]_3$ inevitably afforded γ -deprotonation of the hexamethyldisilazane ligand. By using the uranium precursor $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2(\text{DME})$, we have now obtained multiple

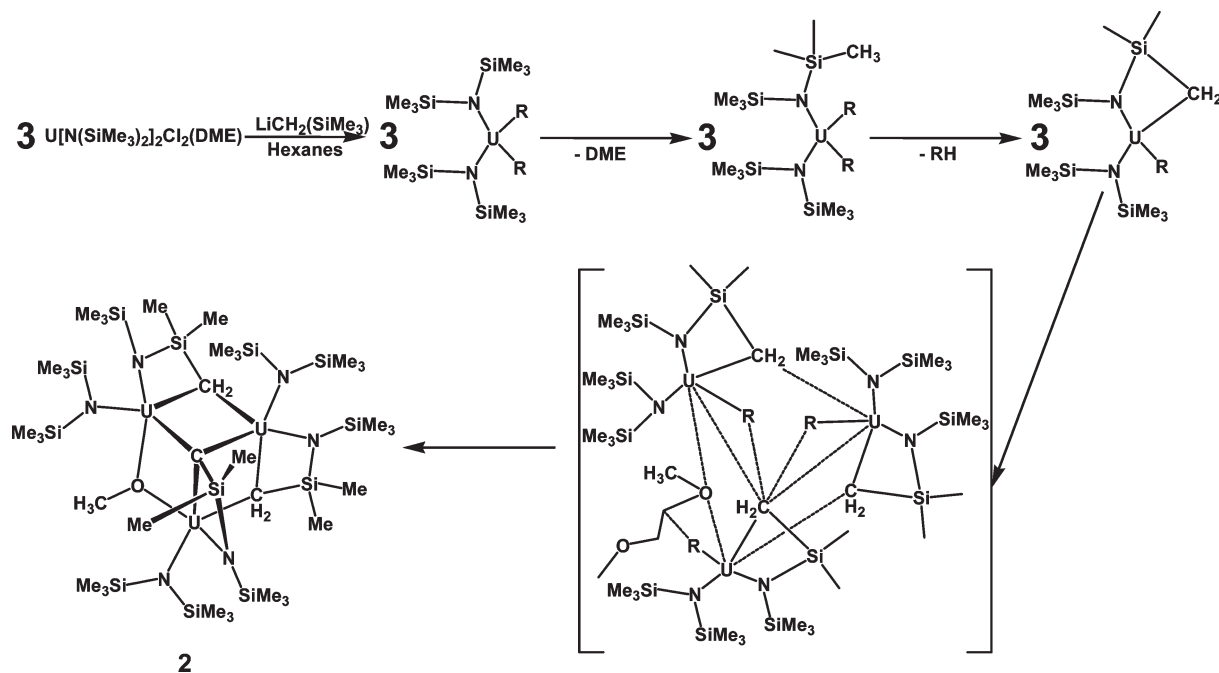
(23) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(24) Sheldrick, G. M. Bruker AXS: Madison, WI, 2001.

Scheme 1



Scheme 2



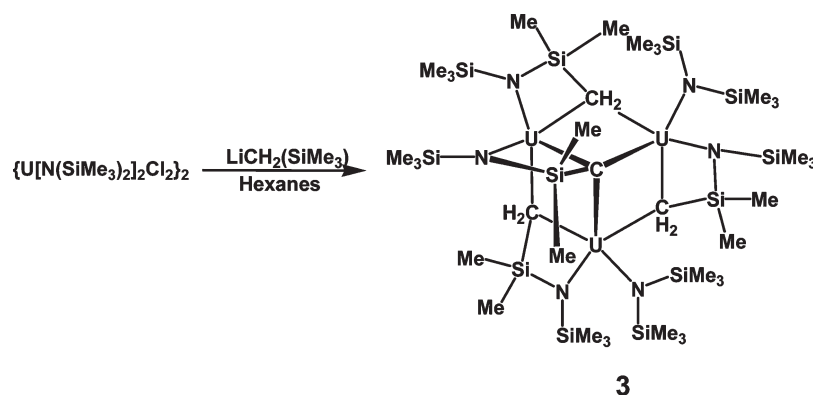
deprotonation and even reduction to the trivalent state depending on the nature of the organo-lithium employed. For example, low temperature reaction with two equivalents of methyl lithium gave the *trivalent* $\{U[(\mu-CH_2-SiMe_2)N(SiMe_3)]_2[\mu-Li(DME)]\}_2$ (**1**) in near to quantitative yield (Scheme 1). Complex **1** does not contain terminal U–Me functions but had both silazanate groups deprotonated at one methyl group forming methylenes. The presence of the lithium counteranion coordinated to the two methylenes implies reduction of the metal center to the trivalent state. The reaction was accompanied by formation of methane (observed in the reaction mixtures of experiments performed in sealed NMR tubes). The 1H NMR spectrum of **1** was in agreement with the formulation as yielded by the crystal structure showing the expected three broad singlets at -13.1 , -28.6 , and -47.0 ppm with a relative intensity of 6:9:2 and respectively assigned to the $Si-(Me)_2$, $N-SiMe_3$, and $-CH_2-$ groups. The resonances of the coordinated DME were located at 3.12 ppm and 3.30 ppm. Degradation of **1** in a Toepler pump apparatus did not yield hydrogen gas, thus excluding the possibility for the complex to be a hydride derivative.

The formation of **1** implies two C–H σ -bond metathetic events of two silazanate Me groups by two incoming Me

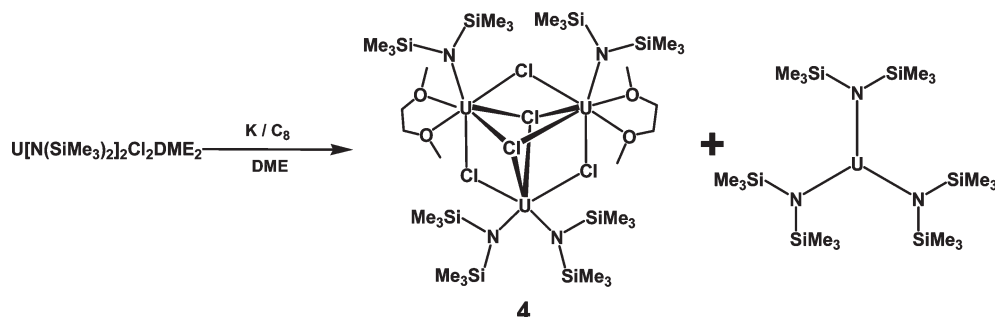
groups and also the intervention of a third equivalent of alkyl-lithium, exclusively acting as a reducing agent. The C–H σ -bond metathesis of silazanate groups by several reagents is widely preceded in actinide chemistry.¹⁵ Attempts to prevent reduction by using a lower amount of MeLi simply decreased the yield of **1**.

A very similar reaction under comparable conditions was carried out in hexane with [(trimethylsilyl) methyl]lithium, affording the trimeric *tetravalent* uranium cluster $\{U[(\mu-CH_2-SiMe_2)N(SiMe_3)][N(SiMe_3)_2]\}_2\{U[(\mu^3-C-SiMe_2)N(SiMe_3)][N(SiMe_3)_2]\}\{\mu-OMe\}$ (**2**) (Scheme 1). The trinuclear structure is composed by three “ $U[N(SiMe_3)_2]$ ” units each bearing another silazanate with different extents of deprotonation. Two units displayed the same single deprotonation and formation of methylene. The third instead has undergone triple deprotonation with formation of a carbyne capping the *triangulo* structure. The crystal structure revealed the unexpected presence of one bridging methoxy group, obviously arising from DME cleavage. The 1H NMR spectrum was in agreement with the formulation showing five broadened singlets in the expected 27:3:54:18:4 ratio. The intense resonance at 29.36 ppm integrating for 27H is assigned to the Me groups of the γ -deprotonated amido ligands. The second peak with the relative intensity of 3H

Scheme 3



Scheme 4



situated at 9.85 ppm is assigned to the bridging methoxy group. The most intense peak of the spectrum positioned at 7.19 ppm (54H) is unequivocally assigned to the 18 Me groups of three unaltered $\text{N}(\text{SiMe}_3)_2$ ligands. Two partly overlapping broad signals centered at -0.13 ppm are assigned to the six $\text{Si}(\text{Me})_2$ units and account for 18 protons. Finally, one remaining signal at -46.90 ppm is attributed to the four protons of the bridging methylene groups. No signs of possible dynamic behavior have been observed at variable temperatures.

At first glance, the formation of **2** seems to be the result of a complex transformation. Instead, it can be easily rationalized by assuming the intermediate formation of three identical $[\text{N}(\text{SiMe}_3)_2][\mu\text{-CH}_2\text{-Si}(\text{Me})_2\text{-N}(\text{SiMe}_3)]\text{UR}$ units. Two alkyls from two units metatesized the same $-\text{CH}_2-$ group of a third unit giving rise to the carbyne. The third U-R group attacked a DME solvent molecule forming the $-\text{OMe}$ group (Scheme 2). Accordingly, the presence of $\text{MeOCH}_2\text{CH}_2\text{CH}_2\text{-SiMe}_3$ in the reaction mixture was detected in the GC-MS of the mother liquor. No reduction of the metal centers occurred in this case as a probable result of the lesser reducing power of the particular lithium-alkyl employed in this case.

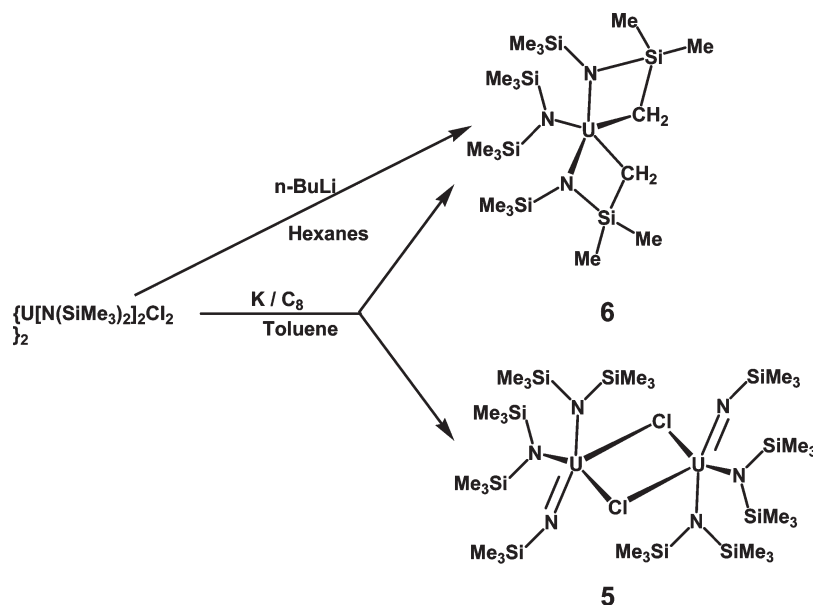
To prevent the interference of DME in the reactivity, a reaction under identical conditions was carried out by using the dimeric and solvent-free $\{\text{U}[\mu\text{-Cl}]\text{Cl}[\text{N}(\text{SiMe}_3)_2]\}_2$ as a starting material. Similar to the transformation described above and despite the poor solubility in hexane of this starting uranium complex, the reaction also occurred very rapidly upon mixing, affording complete solubilization and color change. Black crystals of $\{\text{U}[\mu\text{-(CH}_2\text{-SiMe}_2\text{N}(\text{SiMe}_3))\text{-N}(\text{SiMe}_3)_2]\}_2\{\text{U}[\mu_3\text{-(C-SiMe}_2\text{N}(\text{SiMe}_3))\text{-(CH}_2\text{-SiMe}_2\text{N}(\text{SiMe}_3))]\}$ (**3**) were obtained after a suitable workup (Scheme 3).

Complex **3** is also trimeric with an arrangement of the ligands closely reminiscent of **2**. The main difference consists of the absence of the MeO unit. A similarly triply deprotonated tricapping group also is the salient feature of this structure. This formulation is not only indicated by the geometrical parameters provided by the crystal structure but also by the ^1H NMR spectrum. The higher molecular symmetry results in a simpler spectrum consisting of five resonances in the ratio 6:6:3:1:1. The first resonance is observed at 24.11 ppm and is assigned to the protons of four N-SiMe_3 fragments of γ -deprotonated ligands. The second peak of the same intensity at 7.22 ppm is assigned to four SiMe_3 groups, which belongs to unaltered hexamethyldisilazanate groups. A magnetically different environment for $\text{Si}(\text{Me})_2$ protons of bridging versus tricapped fragments results in the appearance of two peaks at -13.48 ppm and -16.85 ppm with a relative intensity of 3:1. Finally, the last resonance positioned at -43.10 ppm could be assigned to the six protons of three bridging $-\text{CH}_2-$ fragments.

The formation of **3** may be rationalized with the same arguments illustrated in Scheme 2, the only difference being the attack of the third U-R alkyl function of the third unit to the other Si-CH_3 moiety, thus affording the third $\mu\text{-CH}_2-$ unit.

The spontaneous reduction observed during the formation of **1** encouraged us to attempt a more systematic exploration of the reduction chemistry of uranium to probe the ability of the silazanate ligand system to stabilize more reduced species. Reduction of $\text{UCl}_2[\text{N}(\text{SiMe}_3)_2]_2\text{-[DME]}$ with KC_8 in DME proceeds rather slowly, with the reaction being completed after 3 days of stirring at room temperature. The reaction progress was indicated by both the color change of the reaction mixture and the

Scheme 5



disappearance of the characteristic coloration of potassium graphite. After workup and precipitation, the dark red-purple $\{U\text{-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2][\text{DME}]\}_2\{U\text{-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2]\text{-}\{\mu_3\text{-Cl}\}_2$ (**4**) was isolated as a crystalline solid (Scheme 4). The crystal structure revealed a triangular cluster where three uranium atoms are bridged by five chlorides. Two metal centers bear only one silazanate, while the third has retained two. The oxidation state is clearly trivalent, and the ^1H NMR spectrum did not provide any additional information due to very large line broadening and overlapping. Degradation of **4** in a Toepler pump apparatus did not give hydrogen gas, thus excluding the possibility of the complex being a hydride derivative.

The only noticeable feature of this reaction is the ligand dissociation, as partly occurred during the reduction. A variable amount of the tris-silazanate uranium complex accompanied this reaction, thus indicating that ligand scrambling is an important aspect of this transformation.

The presence of DME coordinated to two of the three uranium atoms of the *triangulo* cluster might have a quenching power in the reactivity of the trivalent uranium centers, and thus, we have attempted an identical reduction of the DME-free tetravalent precursor $\{U[\mu\text{-Cl}]\text{Cl}[\text{N}(\text{SiMe}_3)_2]\}_2$ with $\text{K}/\text{graphite}$ in toluene. The reaction took almost seven days to be completed, possibly as a result of the very low solubility of both reagents in toluene. The progress of the reaction was indicated by the disappearance of the characteristic tint of KC_8 as well as the increasing coloration of the mother liquor. Workup of the reaction mixture, followed by fractional crystallization, afforded two separate compounds $\{U\text{-}\mu\text{-Cl}[\text{N}(\text{SiMe}_3)_2][=\text{N}(\text{SiMe}_3)]\}_2$ (**5**) and $U(\mu\text{-CH}_2\text{-SiMe}_2)\text{N}(\text{SiMe}_3)_2[\text{N}(\text{SiMe}_3)_2]$ (**6**), both containing the metal center in its pentavalent state (Scheme 5).

The formation of **5** implies acquisition of one additional silazanate and cleavage of one of them to form a terminally bonded imido group with the dinuclear core assembled via a residual bridging chlorine atom. The imido group forms the expected short bond distance with the metal but deviates significantly from linearity (160.5°). The IR spectrum, however, neatly excluded the possible

presence of hydrogen bonded to the N atom. Unfortunately, the NMR was uninformative due to severe line broadening and overlapping, but the low magnetic moment [$\mu_{\text{eff}} = 2.18 \mu_{\text{B}}$ per dimetallic unit] was in the expected range.

Complex **6** instead appears to be the result of the acquisition of one additional silazanate, γ -metalation of two methyl groups, and two-electron oxidation. Even in this case, the NMR spectrum was uninformative, but the magnetism [$\mu_{\text{eff}} = 1.48 \mu_{\text{B}}$] was in agreement with the electronic configuration of a monomeric pentavalent uranium complex.

The formation of both compounds containing uranium in the rather unusual pentavalent state and from a *reduction* carried out with a strong reducing reagent such as KC_8 is surprising. It can be explained only by assuming the formation of transient reduced species followed by reoxidation at the expense of the silazanate ligand system. In addition, the acquisition of the third ligand possibly indicates the occurrence of a disproportionative pathway. In the case of complex **5**, the reoxidation resulted in the *formal* elimination of one $-\text{SiMe}_3$ group with formation of the imido function. The formation of **6** instead implies a *formal* elimination of H_2 from $U[\text{N}(\text{SiMe}_3)_2]_3$, although the reaction must follow a different pathway, given that $U[\text{N}(\text{SiMe}_3)_2]_3$ is a stable compound. However, no hydrogen gas was detected when experiments were carried out in a sealed vessel connected to a Toepler pump. While a rationalization for the formation of **5** is rather straightforward, the formation of **6** is more puzzling. The same complex may also be generated upon treatment of the same starting material with two equivalents of $n\text{-BuLi}$, the use of which as both alkylating and reducing agent is common knowledge in transition metal chemistry. In analogy with the formation of **1**, we reasoned that alkylation of $\{U[\mu\text{-Cl}]\text{Cl}[\text{N}(\text{SiMe}_3)_2]\}_2$ with two equivalent of $n\text{-BuLi}$ may cause the double γ -metalation of the two silazanate ligands. The oxidation to the pentavalent state and the acquisition of the third silazanate may instead be achieved via disproportionation of an intermediate trivalent species. The identities of the byproducts of these reactions remain so far unknown.

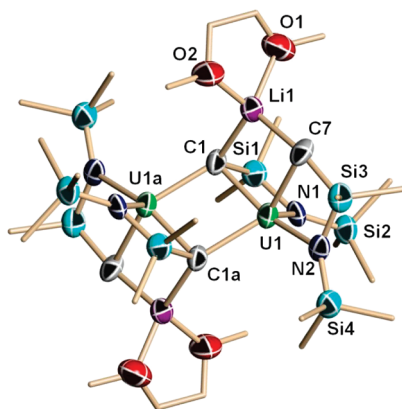


Figure 1. Thermal ellipsoid diagrams of **1** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms, methyl carbon atoms of SiMe_3 units, and thermal ellipsoids of some carbon atoms have been omitted for clarity. Symmetry operator: $-1, 0, 0/0, -1, 0/0, 0, -1$.

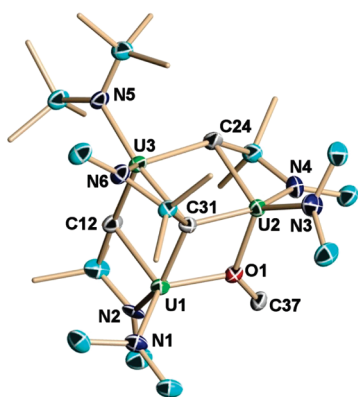


Figure 2. Thermal ellipsoid diagrams of **2** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms, methyl carbon atoms of some SiMe_3 units, and thermal ellipsoids of some carbon atoms have been omitted for clarity.

Crystal Structure Descriptions

Complex 1. The crystal structure of **1** comprises a symmetry generated dimer formed by two uranium and two lithium centers surrounded by four deprotonated silazane ligands. The sharing by uranium of one of its $\mu\text{-CH}_2$ groups with the second uranium center of an identical unit and with one lithium cation assembles the polymetallic structure. Each uranium atom resides in the center of a distorted trigonal bipyramidal environment. One axial position of the bipyramid is occupied by the nitrogen atom of a methylene-pentamethyldisilazane fragment [$\text{U}(1)\text{--N}(2) = 2.296(10)$ Å, $\text{N}(2)\text{--U}(1)\text{--C}(1) = 161.1(4)^\circ$], whose methylene group located in the equatorial position [$\text{U}(1)\text{--C}(7) = 2.518(13)$ Å, $\text{C}(7)\text{--U}(1)\text{--C}(1) = 90.9(4)^\circ$] bridges one lithium center. The other axial position is occupied by the methylene of the second deprotonated silazane ligand which bridges the second uranium and the lithium atom. The corresponding nitrogen occupies the second equatorial position [$\text{U}(1)\text{--C}(1) = 2.362(12)$ Å, $\text{U}(1)\text{--N}(1) = 2.302(10)$ Å, $\text{C}(7)\text{--U}(1)\text{--N}(1) = 111.7(4)^\circ$, $\text{C}(1)\text{--U}(1)\text{--N}(1) = 79.0(3)^\circ$] (Figure 1). The last equatorial position is occupied by the bridging methylene of the symmetry generated unit [$\text{U}(1)\text{--C}(1\text{A}) = 2.372(10)$ Å, $\text{C}(1\text{A})\text{--U}(1)\text{--C}(7) = 131.9(4)^\circ$, $\text{C}(1\text{A})\text{--U}(1)\text{--C}(1) = 80.4(4)^\circ$]. The uranium metric parameters com-

pare well with those of other actinide silazane complexes.¹⁵

Complex 2. The crystal structure of **2** reveals a trinuclear cluster consisting of three uranium metal centers, each bearing one intact and one deprotonated silazane ligand. One methoxide group bridging two of the three uranium centers completes the structure. The other three silazane groups are deprotonated to different extents. Two are singly deprotonated, each bridging one pair of uranium atoms with the methylene groups. The third appears to be triply deprotonated with the carbyne group bridging the three uranium atoms. Each of the uranium atoms is located at the center of a trigonal bipyramid. One of the axial positions of each bipyramid is occupied by the shared μ^3 -carbyne carbon atom [$\text{U}(1)\text{--C}(31) = 2.362(19)$ Å, $\text{U}(2)\text{--C}(31) = 2.284(19)$ Å, $\text{U}(3)\text{--C}(31) = 2.415(6)$ Å] (Figure 2).

One of the three uranium metals has the nitrogen donor atom of the unaltered hexamethyldisilazane in the second axial position [$\text{U}(3)\text{--N}(5) = 2.313(16)$ Å, $\text{N}(5)\text{--U}(3)\text{--C}(31) = 171.8(6)^\circ$]. Instead both $\text{U}(1)$ and $\text{U}(2)$ bear in the second axial position a nitrogen donor atom of the amido-methylene ligands [$\text{U}(1)\text{--N}(2) = 2.240(15)$ Å, $\text{U}(2)\text{--N}(4) = 2.231(15)$ Å, $\text{C}(31)\text{--U}(1)\text{--N}(2) = 147.6(5)^\circ$, $\text{C}(31)\text{--U}(2)\text{--N}(4) = 145.2(5)^\circ$]. Both atoms also have one of their equatorial positions occupied by the nitrogen of one intact hexamethyldisilazane unit [$\text{U}(1)\text{--N}(1) = 2.289(15)$ Å, $\text{N}(1)\text{--U}(1)\text{--N}(2) = 100.8(5)^\circ$, $\text{U}(2)\text{--N}(3) = 2.323(15)$ Å, $\text{N}(3)\text{--U}(2)\text{--N}(4) = 103.6(6)^\circ$]. Their second equatorial positions are occupied by the oxygen atom of the bridging methoxy group [$\text{U}(1)\text{--O}(1) = 2.288(12)$ Å, $\text{U}(2)\text{--O}(1) = 2.313(13)$ Å, $\text{O}(1)\text{--U}(1)\text{--N}(1) = 126.4(5)^\circ$, $\text{O}(1)\text{--U}(1)\text{--N}(2) = 97.7(5)^\circ$, $\text{O}(1)\text{--U}(2)\text{--N}(3) = 124.9(5)^\circ$, $\text{O}(1)\text{--U}(2)\text{--N}(4) = 90.3(5)^\circ$, $\text{U}(1)\text{--O}(1)\text{--U}(2) = 107.0(5)^\circ$], while the third sites are occupied by the bridging methylene groups of the two methylene-pentamethyldisilazane ligands [$\text{U}(1)\text{--C}(12) = 2.62(2)$ Å, $\text{C}(12)\text{--U}(1)\text{--N}(1) = 128.9(6)^\circ$, $\text{C}(12)\text{--U}(1)\text{--N}(2) = 69.0(6)^\circ$, $\text{U}(2)\text{--C}(24) = 2.62(2)$ Å, $\text{C}(24)\text{--U}(2)\text{--N}(3) = 129.4(6)^\circ$, $\text{C}(24)\text{--U}(2)\text{--N}(4) = 70.9(6)^\circ$]. In turn, the $\text{U}(3)$ center has the two above methylene groups occupying the two equatorial positions [$\text{U}(3)\text{--C}(12) = 2.57(2)$ Å, $\text{U}(3)\text{--C}(24) = 2.66(2)$ Å, $[\text{U}(1)\text{--C}(12)\text{--U}(3) = 90.9(6)^\circ$, $\text{U}(2)\text{--C}(24)\text{--U}(3) = 90.1(6)^\circ$; $\text{C}(12)\text{--U}(3)\text{--C}(24) = 94.8(7)^\circ$, $\text{C}(12)\text{--U}(3)\text{--N}(5) = 101.5(6)^\circ$, $\text{C}(24)\text{--U}(3)\text{--N}(5) = 92.5(6)^\circ$], the last being occupied by the nitrogen atom of the carbyne-amido ligand [$\text{U}(3)\text{--N}(6) = 2.261(15)$ Å, $\text{N}(6)\text{--U}(3)\text{--N}(5) = 107.1(6)^\circ$, $\text{N}(6)\text{--U}(3)\text{--C}(12) = 119.8(6)^\circ$]. Even in this case, the $\text{U}\text{--C}$ and $\text{U}\text{--N}$ distances compare well with those of other actinide silazane complexes.¹⁵

Complex 3. Complex **3** also is a trimetallic cluster with a structure reminiscent of **2**, being composed by three silazane units and three additional silazanes deprotonated to different extents. The main difference with **2** consists of the replacement of the $\mu\text{-OMe}$ group with a $\mu\text{-methylene}$ moiety. As in **2**, each U metal center lies in the center of a trigonal bipyramid with one common axial position occupied by the tetrahedral carbyne carbon atom $\text{C}(31)$ μ^3 -bonded to the three uranium metal centers [$\text{U}(1)\text{--C}(31) = 2.361(4)$ Å, $\text{U}(2)\text{--C}(31) = 2.352(5)$ Å, $\text{U}(3)\text{--C}(31) = 2.339(4)$ Å] (Figure 3).

Each U metal center has the nitrogen donor atom from each of three γ -metalated-amido units in its second axial

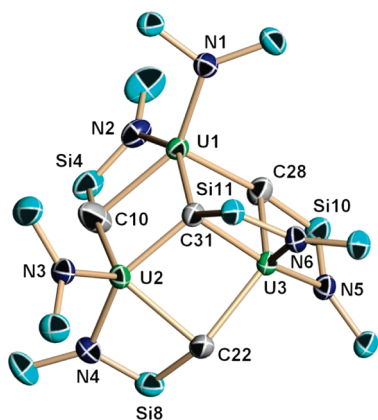


Figure 3. Partial thermal ellipsoid diagrams of **3** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms, methyl carbon atoms of some SiMe_3 units, and thermal ellipsoids of some carbon atoms have been omitted for clarity.

position [$\text{U}(1)-\text{N}(2) = 2.286(4) \text{ \AA}$, $\text{U}(2)-\text{N}(4) = 2.276(4) \text{ \AA}$, $\text{U}(3)-\text{N}(5) = 2.275(4) \text{ \AA}$, $\text{N}(2)-\text{U}(1)-\text{C}(31) = 144.23(16)^\circ$, $\text{N}(4)-\text{U}(2)-\text{C}(31) = 141.06(15)^\circ$, $\text{N}(5)-\text{U}(3)-\text{C}(31) = 153.21(15)^\circ$]. The three methylene atoms bridge a pair of uranium centers each [$\text{U}(1)-\text{C}(10) = 2.658(6) \text{ \AA}$, $\text{C}(10)-\text{U}(2) = 2.557(6) \text{ \AA}$, $\text{U}(2)-\text{C}(22) = 2.677(5) \text{ \AA}$, $\text{C}(22)-\text{U}(3) = 2.602(5) \text{ \AA}$, $\text{U}(3)-\text{C}(28) = 2.634(5) \text{ \AA}$, $\text{C}(28)-\text{U}(1) = 2.553(5) \text{ \AA}$] occupying equatorial positions of two neighboring U metal centers [$\text{C}(10)-\text{U}(1)-\text{C}(31) = 78.71(18)^\circ$, $\text{C}(10)-\text{U}(1)-\text{C}(28) = 105.29(17)^\circ$, $\text{C}(22)-\text{U}(2)-\text{C}(31) = 81.08(15)^\circ$, $\text{C}(10)-\text{U}(2)-\text{C}(22) = 112.60(17)^\circ$, $\text{C}(28)-\text{U}(3)-\text{C}(31) = 84.05(15)^\circ$, $\text{C}(22)-\text{U}(3)-\text{C}(28) = 124.81(16)^\circ$] and assembling the trimeric unit [$\text{U}(1)-\text{C}(10)-\text{U}(2) = 93.06(18)^\circ$, $\text{U}(2)-\text{C}(22)-\text{U}(3) = 89.15(19)^\circ$, $\text{U}(3)-\text{C}(28)-\text{U}(1) = 89.03(18)^\circ$]. The last equatorial positions in the coordination polyhedra of two uranium metal centers are occupied by two nitrogen donor atoms of two unaltered hexamethyldisilazane ligands [$\text{U}(1)-\text{N}(1) = 2.303(4) \text{ \AA}$, $\text{N}(1)-\text{U}(1)-\text{C}(31) = 106.97(15)^\circ$, $\text{N}(1)-\text{U}(1)-\text{C}(10) = 147.6(2)^\circ$, $\text{U}(2)-\text{N}(3) = 2.315(4) \text{ \AA}$, $\text{N}(3)-\text{U}(2)-\text{C}(31) = 113.12(15)^\circ$, $\text{N}(3)-\text{U}(2)-\text{C}(22) = 129.25(15)^\circ$]. The last equatorial position of the third uranium is occupied by the nitrogen atom of the same carbyne-pentamethyldisilazane unit [$\text{U}(3)-\text{N}(6) = 2.223(4) \text{ \AA}$, $\text{N}(6)-\text{U}(3)-\text{C}(31) = 75.97(15)^\circ$, $\text{N}(6)-\text{U}(3)-\text{C}(28) = 121.32(16)^\circ$].

Complex 4. The structure of **4** is also trimeric but with the three uranium metal centers bridged by five chlorine atoms. Three are each bridging one pair of metals forming a rather planar U_3Cl_3 core [$\text{U}(1)-\text{Cl}(1) = 2.841(5) \text{ \AA}$, $\text{U}(1)-\text{Cl}(2) = 2.809(5) \text{ \AA}$, $\text{U}(2)-\text{Cl}(1) = 2.843(4) \text{ \AA}$, $\text{U}(2)-\text{Cl}(3) = 2.812(4) \text{ \AA}$, $\text{U}(3)-\text{Cl}(3) = 2.875(5) \text{ \AA}$, $\text{U}(3)-\text{Cl}(2) = 2.891(5) \text{ \AA}$, $\text{Cl}(1)-\text{U}(1)-\text{Cl}(4) = 72.45(12)^\circ$, $\text{Cl}(2)-\text{U}(1)-\text{Cl}(4) = 73.57(13)^\circ$, $\text{Cl}(1)-\text{U}(1)-\text{Cl}(5) = 75.52(13)^\circ$, $\text{Cl}(2)-\text{U}(1)-\text{Cl}(5) = 76.39(13)^\circ$], while the other two are placed in apical positions on the two opposite sides of the U_3Cl_3 plane, each being μ^3 -bonded to the three metals [$\text{U}(1)-\text{Cl}(4) = 3.103(5) \text{ \AA}$, $\text{U}(1)-\text{Cl}(5) = 2.885(4) \text{ \AA}$, $\text{Cl}(4)-\text{U}(1)-\text{Cl}(5) = 68.51(12)^\circ$, $\text{U}(2)-\text{Cl}(4) = 2.879(4) \text{ \AA}$, $\text{U}(2)-\text{Cl}(5) = 3.068(5) \text{ \AA}$, $\text{Cl}(4)-\text{U}(2)-\text{Cl}(5) = 69.09(12)^\circ$, $\text{U}(3)-\text{Cl}(4) = 3.074(5) \text{ \AA}$, $\text{U}(3)-\text{Cl}(5) = 3.065(4) \text{ \AA}$, $\text{Cl}(4)-\text{U}(3)-\text{Cl}(5) = 66.71(12)^\circ$]. The three metals reside in different coordination environments. Two have the same heavily distorted pentagonal bipyramidal geometry with

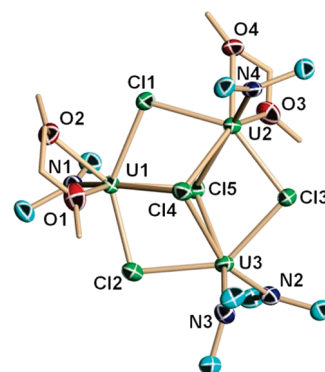


Figure 4. Partial thermal ellipsoid diagrams of **4** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms, methyl carbon atoms of some SiMe_3 units, and thermal ellipsoids for all carbon atoms have been omitted for clarity.

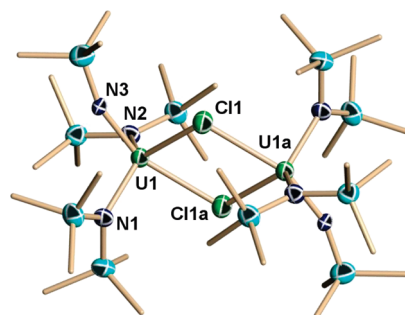


Figure 5. Partial thermal ellipsoid diagrams of **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids for all carbon atoms have been omitted for clarity. Symmetry operator: $-1, 0, 0/0, -1, 0/0, 0, -1$.

four coordination sites occupied by the four bridging chlorine atoms, two by the oxygen of one coordinated DME [$\text{U}(1)-\text{O}(1) = 2.593(13) \text{ \AA}$, $\text{U}(1)-\text{O}(2) = 2.592(12) \text{ \AA}$, $\text{O}(1)-\text{U}(1)-\text{Cl}(4) = 71.5(3)^\circ$, $\text{O}(2)-\text{U}(1)-\text{Cl}(4) = 112.5(3)^\circ$, $\text{O}(1)-\text{U}(1)-\text{Cl}(2) = 84.3(3)^\circ$, $\text{O}(2)-\text{U}(1)-\text{Cl}(1) = 72.0(3)^\circ$], and the last by the nitrogen atom of one intact silazanate group [$\text{U}(1)-\text{N}(1) = 2.298(14) \text{ \AA}$, $\text{N}(1)-\text{U}(1)-\text{Cl}(4) = 163.9(3)^\circ$, $\text{U}(2)-\text{N}(4) = 2.304(14) \text{ \AA}$, $\text{N}(4)-\text{U}(2)-\text{Cl}(4) = 96.7(3)^\circ$]. The third U atom is located instead in the center of a distorted octahedron with four coordination sites occupied by the bridging chlorine atoms and two nitrogen atoms of two intact silazanate located in the two remaining *cis* positions [$\text{N}(2)-\text{U}(3)-\text{N}(2) = 104.10(12)^\circ$] (Figure 4).

Complex 5. Complex **5** is dimeric and consists of two identical uranium-containing units bridged by two chlorine atoms. The coordination geometry of uranium is distorted trigonal bipyramidal with the axial positions occupied by one bridging chloride [$\text{U}(1)-\text{Cl}(1) = 2.829(2) \text{ \AA}$, $\text{Cl}(1)-\text{U}(1)-\text{Cl}(1A) = 72.79(6)^\circ$, $\text{U}(1)-\text{Cl}(1)-\text{U}(1A) = 107.21(6)^\circ$] and the second by the imido nitrogen atom [$\text{U}(1)-\text{N}(3) = 2.081(5) \text{ \AA}$, $\text{N}(3)-\text{U}(1)-\text{Cl}(1A) = 154.87(13)^\circ$] (Figure 5).

The two equatorial positions are occupied by the nitrogen atoms of two hexamethyldisilazane ligands [$\text{U}(1)-\text{N}(1) = 2.237(5) \text{ \AA}$, $\text{U}(1)-\text{N}(2) = 2.249(5) \text{ \AA}$, $\text{N}(1)-\text{U}(1)-\text{Cl}(1) = 111.87(14)^\circ$, $\text{N}(2)-\text{U}(1)-\text{Cl}(1) = 126.54(13)^\circ$] and by the second bridging chlorine atom [$\text{U}(1)-\text{Cl}(1A) = 2.847(2) \text{ \AA}$]. The terminally bonded imido group deviates

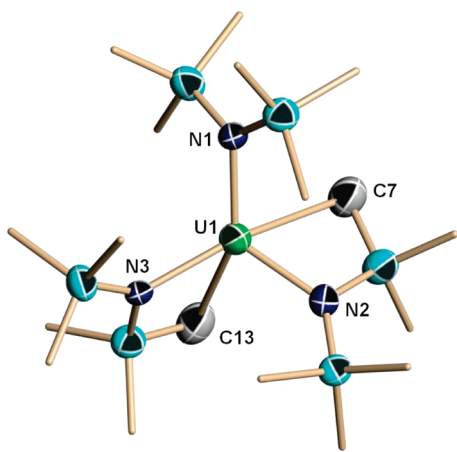


Figure 6. Partial thermal ellipsoid diagrams of **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl carbon atoms of the SiMe_3 units have been omitted for clarity.

from linearity as a possible result of the steric hindrance [$\text{U}(1)\text{--N}(3)\text{--Si}(5) = 160.8(2)^\circ$] and forms the expected short U–N distance [$\text{U}(1)\text{--N}(3) = 2.081(5) \text{ \AA}$].

Complex 6. Complex **6** is monomeric and consists of a single uranium atom located in the center of a distorted trigonal bipyramid, as determined by the carbon and nitrogen atoms of two methylene-pentamethyldisilazane ligands and the nitrogen of one intact silazanate [$\text{C}(13)\text{--U}(1)\text{--N}(3) = 65.7(3)^\circ$, $\text{C}(7)\text{--U}(1)\text{--N}(3) = 149.2(4)^\circ$, $\text{N}(3)\text{--U}(1)\text{--N}(2) = 114.3(2)^\circ$, $\text{C}(13)\text{--U}(1)\text{--N}(2) = 91.3(4)^\circ$]. The first methylene-pentamethyldisilazane ligand occupies one axial position with the nitrogen atom [$\text{U}(1)\text{--N}(3) = 2.258(6) \text{ \AA}$] and one equatorial with the methylene group [$\text{U}(1)\text{--C}(13) = 2.985(19) \text{ \AA}$]. The second has the same arrangement except that the nitrogen and methylene are respectively located on the equatorial

[$\text{U}(1)\text{--N}(2) = 2.241(7) \text{ \AA}$] and axial positions [$\text{U}(1)\text{--C}(7) = 2.830(18) \text{ \AA}$] (Figure 6). The last equatorial position around the U metal center is occupied by the nitrogen donor atom of an unaltered hexamethyldisilazanate ligand [$\text{U}(1)\text{--N}(1) = 2.240(7) \text{ \AA}$, $\text{N}(1)\text{--U}(1)\text{--N}(3) = 113.2(2)^\circ$, $\text{N}(1)\text{--U}(1)\text{--C}(13) = 143.2(4)^\circ$].

Conclusions

Alkylation of DME-solvate and unsolvate forms of $\text{U}[\text{N}(\text{SiMe}_3)_2]_2\text{Cl}_2$ under different reduction conditions resulted in the formation of several γ -deprotonated products with multiple deprotonations having occurred in two cases at the same carbon atom. We have observed that either reduction of the metal center or solvent cleavage may accompany the transformation depending on the reaction conditions. Alkylation with *n*-butyl lithium yielded a surprising pentavalent compound. The formation *under reducing conditions* of a compound with the metal center in an oxidation state higher than in the starting material was accompanied by ligand migration. This possibly hints at the occurrence of a disproportionation of a transient highly reactive low-valent intermediate in addition to its reoxidation at the expense of the ligand.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for complexes **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.