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The Bis Metallacyclic Anion $[U(N\{SiMe_3\}_2)(CH_2SiMe_2N\{SiMe_3\})_2]^-$

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A series of bis metallacyclic compounds $[M(THF)_xUN^*(CH_2SiMe_2N\{SiMe_3\})_2]_n$ [M = Na (**2**), Li (**3**), or K (**4**), $N^* = N(SiMe_3)_2$] were isolated from reactions of UCl_4 or $[UN^*_3Cl]$ with MN* or by treatment of $[UN^*_2(CH_2SiMe_2N\{SiMe_3\})]$ (**1**) or $[UN^*_3]$ with MN*, MH, or $LiCH_2SiMe_3$ in tetrahydrofuran (THF). Crystals of **2a**·1/6*n*-pentane ($x = 0$), **2b** ($x = 1$), **2c** ($x = 2$), and **4b** ($x = 1$) were obtained by crystallization of **2** and **4** from pentane, and $[Na(18\text{-crown-}6)(THF)][UN^*(CH_2SiMe_2N\{SiMe_3\})_2]$ (**2d**) and $[Na(15\text{-crown-}5)][UN^*(CH_2SiMe_2N\{SiMe_3\})_2]$ (**2e**) were formed upon addition of the crown ether. The crystal structures of **2a**−**2e** and **4b** exhibit the same $[UN^*(CH_2SiMe_2N\{SiMe_3\})_2]$ units which are linked to Na or K atoms via methylene or methyl groups, giving either tight cation−anion pairs (**2d** and **2e**) or one-dimensional (1D) or two-dimensional (2D) polymeric compounds with Na or K atoms in bridging position between methylene groups of adjacent units. Reaction of **2** with CO gave the double insertion derivative $[Na_2(THF)U_2N^*_2(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_4]$ (**5b**) and $[Na(15\text{-crown-}5)UN^*(OC\{=CH_2\}\text{-}SiMe_2N\{SiMe_3\})_2]$ (**5c**) in the presence of the crown ether. Thermal decomposition of **5b** gave $[Na_2(THF)U(OC\{=CH_2\}\text{-}SiMe_2N\{SiMe_3\})_3]_2$ (**6**), the product of CO insertion into the putative tris metallacycle $[Na_2(THF)_xU(CH_2SiMe_2N\{SiMe_3\})_3]$. The crystal structures of **5b**, **5c**, and **6** show the interaction of the Na atoms with the exocyclic $C{=}CH_2$ bonds. Diffusion of CO_2 into a THF solution of **2** led to the formation of $[Na(THF)_xUN^*(OC\{O\}CH_2SiMe_2N\{SiMe_3\})_2]$ (**7**) which crystallized from pyridine/pentane to give $[Na(THF)_2(py)_2UN^*(OC\{O\}CH_2SiMe_2N\{SiMe_3\})_2]\cdot 0.5py$ (**8**·0.5py), the first crystallographically characterized complex resulting from CO_2 insertion into a $M(CH_2SiMe_2N\{SiMe_3\})$ metallacycle. Compound **2** reacted with I_2 to give $[UN^*(CH_2SiMe_2N\{SiMe_3\})(N\{SiMe_3\}SiMe_2CH_2I)]$ (**9**) which would represent a new type of so-called "pendulum" systems resulting from a degenerate σ bond metathesis reaction of U−C and C−I bonds.

Introduction

The bis(trimethylsilyl)amide ligand ($N^* = N(SiMe_3)_2$) is ubiquitous in coordination chemistry, and the metal complexes supported by this amide group span the periodic table. This prominent position is favored by the convenient use of the precursor amine which is commercially available as are the corresponding alkali metal amides, but is due above all to the unique properties of the bulky N* ligand which confer to the complexes low coordination numbers with the absence of coordinated solvent molecules, high solubility in hydrocarbons and aromatic solvents, together with a remarkable reactivity.[1] This ligand, which is able to stabilize metal centers in their lowest and highest oxidation states, can be substituted with proton acidic molecules, so that bis(trimethylsilyl)amide compounds are valuable starting materials in inorganic and organometallic syntheses and catalytic cycles. The N* ligand can be converted into a bridging or terminally bonded imido group $=NSiMe_3$ via dissociation of one of the two $SiMe_3$ fragments.[2] A recurrent feature of the $[M(X)N^*]$ complexes is their ready transformation, in the presence of a strong base and/or upon heating conditions, into the metallacycles $[M(\kappa^2(N,C)\text{-}CH_2SiMe_2N\{SiMe_3\})]$ resulting from γ-CH deprotonation and HX elimination.[3] However, double or triple deprotonation of a single silazanate group giving a carbene or carbyne derivative[4] or mono deprotonation of several N* ligands leading to poly metallacycles are very rare.[4,5]

Following the seminal work of Andersen et al. who introduced the N* ligand in uranium chemistry with the synthesis of the uranyl(VI) complex $[UO_2N^*_2(THF)_2]$[6a] and the U(IV) compound $[UN^*_3Cl]$ and its derivatives,[6b] the amido group

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served to prepare a series of uranium complexes in oxidation states varying from +3 to +6.[7] In particular, the uranium(IV) metallacycle $[\mathrm{UN^*_2(CH_2SiMe_2N\{SiMe_3\})}]$[3a,8] (**1**) was found to undergo a variety of organometallic transformations including nucleophilic behavior toward carbonyl molecules and insertion reactions into the U−C bond.[9] While $[\mathrm{ThN^*(Cp^*)}][\mu\text{-}\mathrm{SO_3CF_3}]_3[\mathrm{Th(CH_2SiMe_2N\{SiMe_3\})(Cp^*)}]$,[10a] $[\mathrm{Th(CH_2SiMe_2N\{SiMe_3\})(Ind^*)_2}]$,[10b] and $[\mathrm{U(CH_2SiMe_2N\{SiMe_3\})(Cp^*)_2}]$[7u] (Ind* = permethylindenyl, Cp* = permethylcyclopentadienyl) were the sole actinide complexes with an An-$[\mathrm{CH_2SiMe_2N(SiMe_3)}]$ cycle to have been crystallographically characterized, Korobkov and Gambarotta very recently reported that treatment of $[\mathrm{UN^*_2Cl_2}]$ with organolithium reagents led to the formation of U(III), U(IV), and U(V) metallacycles, with multiple deprotonations sometimes occurring at the same carbon atom.[5] These results prompt us to present our work on the U(IV) bis metallacyclic anion $[\mathrm{UN^*(CH_2SiMe_2N\{SiMe_3\})_2}]^-$, a species of interest for reactivity studies, easily obtained from $\mathrm{UCl_4}$, $[\mathrm{UN^*_3Cl}]$, or $[\mathrm{UN^*_2(CH_2SiMe_2N\{SiMe_3\})}]$. Here we report on the synthesis and crystal structures of a series of bis metallacyclic compounds $[\mathrm{ML}_x\mathrm{UN^*(CH_2SiMe_2N\{SiMe_3\})_2}]$ which differ by the nature of M (Li, Na, or K) and L (tetrahydrofuran (THF) or crown ether). We also describe the insertion reactions of CO and $\mathrm{CO_2}$ into the two metallacycles and the cleavage of the U−C bond of one metallacycle with $\mathrm{I_2}$, leading to $[\mathrm{UN^*(CH_2SiMe_2N\{SiMe_3\})(N\{SiMe_3\}SiMe_2CH_2I)}]$ which undergoes an unprecedented degenerate rearrangement in solution.

Experimental Section

All reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum line techniques or in a glovebox. THF, toluene, and pentane were distilled from Na/K alloy-benzophenone immediately before use. The deuterated solvents (Eurisotop) were dried over Na/K alloy. IR samples were prepared as Nujol mulls between KBr round cell windows, and the spectra recorded on a Perkin-Elmer FT-IR 1725X spectrometer. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). MN* (M = Na, K) was prepared by refluxing MH and 1,1,1,3,3,3-hexamethyldisilazane (Aldrich) in toluene.[11] MH (M = Na, K) (Fluka), CO (Air Liquide) and $\mathrm{CO_2}$ (Messer) were used without purification; $\mathrm{LiCH_2SiMe_3}$ was isolated as a white powder after evaporation of a commercially available 1 M solution in pentane (Aldrich); 18-crown-6 and 15-crown-5 (Fluka) were dried under vacuum before use. $\mathrm{UCl_4}$,[12] $[\mathrm{UN^*_3Cl}]$,[8] $[\mathrm{UN^*_2(CH_2SiMe_2N\{SiMe_3\})}]$[8] (**1**), and $[\mathrm{U(N^*_3)}]$[11a] were synthesized as previously reported.

Synthesis of $[\mathrm{Na(THF)}_x\mathrm{UN^*(CH_2SiMe_2N\{SiMe_3\})_2}]_n$ (2). (a) A flask was charged with $\mathrm{UCl_4}$ (1000 mg, 2.63 mmol) and NaN* (2460 mg, 13.43 mmol) and THF (30 mL) was condensed in. The color of the solution turned brown after a few minutes and green after 2 h while an off-white precipitate was formed. The reaction mixture was stirred for 24 h at 20 °C and the green solution was filtered and evaporated to dryness, leaving an oily green residue which was dried under vacuum for 48 h. Extraction in toluene (40 mL) and evaporation to dryness afforded a green powder of **2** which was washed with pentane (10 mL × 5). The analytically pure compound **2a** ($x = 0$) was obtained after drying under vacuum at 20 °C for 15 h. Yield: 1434 mg (74%). Anal. Calcd for $\mathrm{C_{18}H_{52}N_3Si_6NaU}$: C, 29.21; H, 7.08; N, 5.68; Na, 3.11. Found: C, 28.89; H, 6.93; N, 5.75; Na, 3.21. ^{1}H NMR (THF-d_8, 23 °C): δ 39.77 (s, 18 H, $\mathrm{SiMe_3}$), 32.18 (s, 6 H, $\mathrm{SiMe_2}$), −5.96 (s, 6 H, $\mathrm{SiMe_2}$), −36.96 (s, 18 H, $\mathrm{SiMe_3}$), −286.20 (s, 2 H, $\mathrm{CH_2}$), −297.80 (s, 2 H, $\mathrm{CH_2}$). ^{1}H NMR (THF-d_8, −97 °C): δ 69.61 (s, 18 H, $\mathrm{SiMe_3}$), 58.48 (s, 6 H, $\mathrm{SiMe_2}$), −9.70 (s, 6 H, $\mathrm{SiMe_2}$), −66.58 (s, 18 H, $\mathrm{SiMe_3}$), −512.38 (s, 2 H, $\mathrm{CH_2}$), −528.37 (s, 2 H, $\mathrm{CH_2}$). ^{1}H NMR (toluene-d_8, 23 °C): δ 44.36 (s, 18 H, $\mathrm{SiMe_3}$), 29.95 (s, 6 H, $\mathrm{SiMe_2}$), −4.77 (s, 6 H, $\mathrm{SiMe_2}$), −42.99 (s, 18 H, $\mathrm{SiMe_3}$), −260.70 (s, 2 H, $\mathrm{CH_2}$), −274.43 (s, 2 H, $\mathrm{CH_2}$). Green needles of **2a**·1/6*n*-pentane were obtained by heating an NMR tube containing a suspension of **2a** (10 mg, 0.013 mmol) and NaN* (2.5 mg, 0.013 mmol) in pentane (0.5 mL) at 60 °C for 2 h, and cooling down the solution at room temperature. Green needles of **2b** ($x = 1$) and **2c** ($x = 2$) were formed by heating a suspension of a less thoroughly dried powder of **2** in pentane. While **2a** is insoluble in pentane, the THF containing complexes **2b** and **2c** are partially soluble in this solvent.

(b) A flask was charged with **1** (200 mg, 0.28 mmol) and NaN* (51 mg, 0.28 mmol) and THF (5 mL) was condensed in. The reaction mixture was stirred for 4 h at 20 °C, and the green solution was filtered and evaporated to dryness, leaving a green oily residue which was extracted in toluene (5 mL). Evaporation to dryness afforded a green powder of **2** which was washed with pentane (5 × 5 mL) and dried under vacuum to give **2a**. Yield: 154 mg (75%).

(c) A flask was charged with **1** (900 mg, 1.25 mmol) and NaH (36 mg, 1.5 mmol) in THF (15 mL). The reaction mixture was stirred for 24 h at 20 °C, and the green solution was filtered and

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evaporated to dryness, leaving an oily green residue which was dried under vacuum for 15 h. Extraction in toluene (40 mL) and evaporation to dryness afforded a green powder of **2** which was washed with pentane (10 mL × 5). Compound **2a** ($x = 0$) was obtained after drying under vacuum at 20 °C for 15 h. Yield: 714 mg (77%).

(d) An NMR tube was charged with [UN*$_3$Cl] (10.0 mg, 0.014 mmol) and NaN* (4.9 mg, 0.027 mmol) and THF-d_8 (0.4 mL) was condensed in. The reaction mixture was stirred for 2 h at 20 °C during which the solution turned green. The NMR spectrum showed the quantitative formation of **2**.

Crystals of [Na(18-crown-6)(THF)][UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (2d). An NMR tube was charged with **2a** (11.1 mg, 0.015 mmol) in pentane (0.5 mL), and 18-crown-6 (6.1 mg, 0.022 mmol) was added. The suspension was heated in a sand bath at 80 °C, and well shaped emerald green crystals of **2d** were formed after 3 days.

Synthesis of [Na(15-crown-5)][UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (2e). An NMR tube was charged with **2a** (20.0 mg, 0.027 mmol) in pentane (1 mL). An off-white emulsion was readily observed upon addition of 15-crown-5 (6.4 μL, 0.032 mmol), and a few green crystals of **2e** were deposited in a few minutes. After heating for 3 d at 60 °C, well shaped emerald green crystals of **2e** were obtained in almost quantitative yield. Anal. Calcd for $C_{28}H_{72}N_3O_5Si_6NaU$: C, 35.02; H, 7.56; N, 4.38. Found: C, 34.37; H, 7.14; N, 4.49. ^{1}H NMR (THF-d_8, 23 °C): δ 39.53 (s, 18 H, SiMe$_3$), 31.94 (s, 6 H, SiMe$_2$), 2.33 (s, 20 H, 15-crown-5), -6.22 (s, 6 H, SiMe$_2$), -37.16 (s, 18 H, SiMe$_3$), -286.36 (s, 2 H, CH$_2$), -297.95 (s, 2 H, CH$_2$).

Synthesis of [M(THF)$_x$UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] [M = Li (3), K (4)]. (a) An NMR tube was charged with **1** (20.1 mg, 0.028 mmol) and LiCH$_2$SiMe$_3$ (2.6 mg, 0.028 mmol) in THF-d_8 (0.4 mL). The NMR spectrum which is identical to that of **2** showed the immediate and quantitative formation of **3**.

(b) By following the same procedure as for **2a**, a green powder of [KUN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$]$_n$ (**4a**) was obtained from UCl$_4$ (200 mg, 0.53 mmol) and KN* (530 mg, 2.66 mmol) in THF (10 mL). Yield: 318 mg (80%). The ^{1}H NMR spectrum of **4a** in toluene-d_8 is identical to that of **2a**. Green crystals of **4b** ($x = 1$) were obtained by heating at 80 °C for 2 h a suspension of a less thoroughly dried powder of **4** (10 mg) in pentane (0.5 mL).

(c) An NMR tube was charged with **1** (10.1 mg, 0.014 mmol) and KH (1.1 mg, 0.027 mmol) in THF-d_8 (0.4 mL). The tube was immersed in an ultrasound bath (70 W, 42 kHz) and after 5 h, the NMR spectrum showed the quantitative formation of **4**.

Reactions of [UN*$_3$] with LiCH$_2$SiMe$_3$ or NaN*. (a) An NMR tube was charged with [UN*$_3$] (20.1 mg, 0.028 mmol) and LiCH$_2$SiMe$_3$ (2.6 mg, 0.028 mmol) in THF-d_8 (0.4 mL). After 10 h at 20 °C, the NMR spectrum, identical to that of **2**, showed the almost quantitative formation of **3**. The same reaction in toluene was slow and led to the formation of **1**.

(b) An NMR tube was charged with [UN*$_3$] (20.0 mg, 0.028 mmol) and NaN* (5.1 mg, 0.028 mmol) in THF-d_8 (0.4 mL). After 48 h at 20 °C, the NMR spectrum showed that 80% of [UN*$_3$] were transformed into **2**. The same reaction in toluene was slow and led to the formation of **1**.

Reaction of 2a with LiCH$_2$SiMe$_3$. An NMR tube was charged with **2a** (10.0 mg, 0.013 mmol) and LiCH$_2$SiMe$_3$ (1.3 mg, 0.013 mmol) in THF-d_8 (0.4 mL). After 3 h at 20 °C, the spectrum showed that **2a** was transformed into a major product whose NMR spectrum can be attributed to the trismetallacycle [NaLiU(CH$_2$SiMe$_2$N{SiMe$_3$})$_3$]. ^{1}H NMR (THF-d_8, 23 °C): δ 36.57 (s, 27 H, SiMe$_3$), -25.39 (s, 18 H, SiMe$_2$), -292.26 (s, 6 H, CH$_2$). All attempts at the purification of this product led to degradation. In contrast, **2a** did not react with MN* (M = Na, K), neither at 20 °C nor at 65 °C for many days.

Synthesis of [Na(THF)$_x$UN*(OC{=CH$_2$}SiMe$_2$N{SiMe$_3$})$_2$] (5), Crystals of [Na$_2$(THF)U$_2$N*$_2$(OC{=CH$_2$}SiMe$_2$N{SiMe$_3$})$_4$] (5b), and Crystals of [Na$_2$(THF)U(OC{=CH$_2$}SiMe$_2$N{SiMe$_3$})$_3$] (6). (a) A 25 mL flask was charged with **2a** (156 mg, 0.211 mmol) in THF (10 mL) and after elimination of argon, the flask was filled with CO (1 atm). The fading of the green solution was observed and after stirring for 5 h at 20 °C, evaporation to dryness afforded a pale green powder of **5**. Further drying under vacuum at 20 °C gave **5a** ($x = 0$). Yield: 168 mg (100%). Anal. Calcd for $C_{20}H_{52}N_3O_2Si_6NaU$: C, 30.17; H, 6.58; N, 5.28; Na, 2.89. Found: C, 29.27; H, 6.23; N, 5.01; Na, 2.83. ^{1}H NMR (THF-d_8, 23 °C): δ 85.27 (s, 2 H, CH$_2$), 54.00 (s, 2 H, CH$_2$), -0.01 (s, 6 H, SiMe$_2$), -14.48 (s, 18 H, SiMe$_3$), -19.01 (s, 18 H, SiMe$_3$), -23.76 (s, 6 H, SiMe$_2$). ^{1}H NMR (THF-d_8, -107 °C): δ 20.8 (s, $w_{1/2}$ = 170 Hz, 2 H, CH$_2$), 17.30 (s, $w_{1/2}$ = 50 Hz, 6 H, SiMe$_2$), 15.4 (s, $w_{1/2}$ = 400 Hz, 2 H, CH$_2$), 1.75 (s, 6 H, SiMe$_2$), -1.55 (s, $w_{1/2}$ = 65 Hz, 18 H, SiMe$_3$), -4.33 (s, $w_{1/2}$ = 45 Hz, 18 H, SiMe$_3$). The variations in the chemical shifts indicate the presence of a rapid equilibrium between the two *cis* and *trans* isomers whose relative proportions strongly vary with the temperature. IR (Nujol): ν/cm^{-1} 1569 m (C=CH$_2$).

(b) An NMR tube was charged with **5** (70 mg, 0.088 mmol) in pentane (0.5 mL). The suspension was heated for 24 h at 100 °C, affording large emerald green crystals of **6**. Yield: 7.0 mg (9%). *Fac*-isomer: ^{1}H NMR (THF-d_8, 23 °C): δ 13.37 (s, $w_{1/2}$ = 120 Hz, 3 H, CH$_2$), 12.85 (s, $w_{1/2}$ = 150 Hz, 3 H, CH$_2$), 1.20 (s, 18 H, SiMe$_2$), -5.80 (s, $w_{1/2}$ = 85 Hz, 27 H, SiMe$_3$). *Mer*-isomer: ^{1}H NMR (THF-d_8, -77 °C): δ 6.94 (s, 3 H, CH$_2$), 4.41 (s, 3 H, CH$_2$), 1.28 (s, 9 H, SiMe$_2$), 1.06 (s, 9 H, SiMe$_2$), -0.82 (s, 27 H, SiMe$_3$). At intermediate temperatures, the two isomers coexist. By following the same procedure but only in one experiment, a few small green crystals of **5b** were obtained together with many larger well-shaped green crystals of the tris metallacycle **6**.

Synthesis of [Na(15-crown-5)UN*(OC{=CH$_2$}SiMe$_2$N{SiMe$_3$})$_2$] (5c). An NMR tube was charged with **5a** (19.9 mg, 0.025 mmol) in pentane (1 mL). An off-white emulsion was readily observed upon addition of 15-crown-5 (5.0 μL, 0.025 mmol), and a crystalline solid was deposited within a few min. The tube was heated for 3 d at 60 °C, leading to the formation of well shaped pale blue crystals of **5c**. Yield: 22 mg (80%). Addition of excess crown ether led to the formation of an oil. Anal. Calcd for $C_{30}H_{72}N_3O_7Si_6NaU$: C, 35.45; H, 7.14; N, 4.13. Found: C, 35.19; H, 7.39; N, 4.33. ^{1}H NMR (THF-d_8, 23 °C): δ 84.19 (s, 2 H, CH$_2$), 54.46 (s, 2 H, CH$_2$), 4.76 (s, 20 H, 15-crown-5), 0.27 (s, 6 H, SiMe$_2$), -14.19 (s, 18 H, SiMe$_3$), -19.08 (s, 18 H, SiMe$_3$), -23.39 (s, 6 H, SiMe$_2$).

Synthesis of [Na(THF)$_x$UN*(OC{O}CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (7) and Crystals of [Na(THF)$_2$(py)$_2$UN*(OC{O}CH$_2$SiMe$_2$N{SiMe$_3$})$_2$]·0.5py (8·0.5py). (a) A 50 mL flask was charged with **2a** (303 mg, 0.409 mmol) in THF (25 mL) and after elimination of argon, the flask was filled with CO$_2$ (1 atm). The color of the solution turned pale blue, and a precipitate was formed in a few minutes. After 30 min at 20 °C and without stirring, the pale blue needles of **7** were filtered off and washed with THF (20 mL × 2). The pale blue powder of **7a** ($x = 0$) was obtained after drying under vacuum at 20 °C. Yield: 203 mg (60%). Anal. Calcd for $C_{20}H_{52}N_3O_4Si_6NaU$: C, 29.01; H, 6.33; N, 5.07; Na, 2.78. Found: C, 28.87; H, 6.23; N, 4.99; Na, 2.70. The ^{1}H NMR spectrum in pyridine-d_5 at 23 °C exhibits broad signals. ^{1}H NMR (pyridine-d_5, -37 °C) isomer 1: δ 13.61 (s, 6 H, SiMe$_2$), 10.92 (s, 2 H, CH$_2$), -7.93 (s, 2 H, CH$_2$), -20.26 (s, 18 H, SiMe$_3$), -35.30 (s, 18 H, SiMe$_3$), -37.32 (s, 6 H, SiMe$_2$); isomer 2: δ 1.92 (s, 6 H, SiMe$_2$), -13.72 (s, 2 H, CH$_2$), -14.37 (s, 18 H, SiMe$_3$), -18.47 (s, 18 H, SiMe$_3$), -42.15 (s, 6 H, SiMe$_2$), -76.21 (s, 2 H, CH$_2$). The ratio isomer 1/isomer 2 is equal to 2. Dissolution of the blue needles of **7** in THF under CO$_2$ atmosphere was observed after 24 h, giving a green solution of unidentified product(s).

(b) An NMR tube was charged with **7** (ca. 5 mg) in pyridine (0.1 mL). Diffusion of pentane into the solution led to the formation of a few green crystals of **8**·0.5py. Rapid desolvation of these crystals was observed at 20 °C. IR (Nujol): ν/cm^{-1} 1629s, 1583 m (OC=O).

Synthesis of [UN*(CH$_2$SiMe$_2$N{SiMe$_3$})(N{SiMe$_3$}SiMe$_2$CH$_2$I)] (9). A flask was charged with **2a** (100 mg, 0.135 mmol) and I$_2$ (34.0 mg, 0.135 mmol) and THF (15 mL) was condensed in.

Table 1. Crystal Data and Structure Refinement Details

	2a·1/6*n*-pentane	**2b**	**2c**	**2d**	**2e**
chemical formula	$C_{18.83}H_{54}N_3NaSi_6U$	$C_{22}H_{60}N_3NaOSi_6U$	$C_{26}H_{68}N_3NaO_2Si_6U$	$C_{34}H_{84}N_3NaO_7Si_6U$	$C_{28}H_{72}N_3NaO_5Si_6U$
M (g mol^{-1})	752.21	812.29	884.39	1076.60	960.45
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	31.313(2)	8.5677(6)	8.5005(3)	11.8259(3)	12.0093(5)
b (Å)	15.4638(6)	40.256(5)	35.152(2)	23.7820(11)	18.4274(13)
c (Å)	23.0146(16)	22.157(3)	14.3900(10)	19.1125(8)	20.8751(17)
α (deg)	90	90	90	90	90
β (deg)	105.402(3)	92.334(7)	101.310(4)	90.065(3)	90
γ (deg)	90	90	90	90	90
V (Å^3)	10743.9(11)	7635.6(15)	4216.4(4)	5375.3(4)	4619.7(5)
Z	12	8	4	4	4
D_{calcd} (g cm^{-3})	1.395	1.413	1.393	1.330	1.381
μ(Mo Kα) (mm^{-1})	4.756	4.469	4.055	3.200	3.711
F(000)	4500	3264	1792	2208	1952
reflns collcd	138401	123141	91558	113083	98017
indep reflns	19619	13397	8003	10182	8727
obsd reflns [$I > 2\sigma(I)$]	12840	6465	6109	7918	7381
R_{int}	0.073	0.055	0.046	0.036	0.037
params refined/restraints	875/12	643/69	368/0	484/184	414/0
R1	0.051	0.052	0.027	0.046	0.044
wR2	0.087	0.076	0.048	0.112	0.067
S	0.984	0.906	0.967	1.028	1.065
$\Delta\rho_{min}$ (e Å^{-3})	−1.01	−1.02	−0.96	−1.00	−0.96
$\Delta\rho_{max}$ (e Å^{-3})	0.98	0.90	0.52	1.94	0.57

	4b	**5b**	**5c**	**6**	**8**·0.5pyridine
chemical formula	$C_{22}H_{60}KN_3OSi_6U$	$C_{44}H_{112}N_6Na_2O_5Si_{12}U_2$	$C_{30}H_{72}N_3NaO_7Si_6U$	$C_{25}H_{59}N_3Na_2O_4Si_6U$	$C_{40.5}H_{80.5}N_{5.5}NaO_6Si_6U$
M (g mol^{-1})	828.40	1664.52	1016.47	918.30	1170.16
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$
a (Å)	11.8047(5)	11.8946(6)	36.9607(19)	31.9245(11)	16.0569(11)
b (Å)	14.0356(5)	16.6639(9)	11.0587(5)	12.0922(7)	19.7051(19)
c (Å)	23.6273(8)	20.5219(7)	24.2187(11)	24.1499(13)	18.6003(15)
α (deg)	90	75.711(3)	90	90	90
β (deg)	90	80.618(3)	103.147(3)	117.776(3)	97.394(5)
γ (deg)	90	75.128(2)	90	90	90
V (Å^3)	3914.7(3)	3788.1(3)	9639.6(8)	8248.6(7)	5836.3(8)
Z	4	2	8	8	4
D_{calcd} (g cm^{-3})	1.406	1.459	1.401	1.479	1.332
μ(Mo Kα) (mm^{-1})	4.454	4.509	3.565	4.161	2.954
F(000)	1664	1664	4128	3680	2388
reflns collcd	65251	176841	318661	125258	185179
indep reflns	7397	14381	18244	7821	11000
obsd reflns [$I > 2\sigma(I)$]	6673	11747	10732	5862	6474
R_{int}	0.032	0.041	0.065	0.051	0.041
params refined/restraints	322/0	670/30	897/195	385/12	545/240
R1	0.029	0.030	0.059	0.032	0.076
wR2	0.067	0.071	0.144	0.064	0.236
S	1.036	1.012	1.066	0.968	1.039
$\Delta\rho_{min}$ (e Å^{-3})	−0.69	−1.24	−1.18	−1.00	−0.98
$\Delta\rho_{max}$ (e Å^{-3})	0.59	0.67	2.31	0.69	1.32

After stirring for 20 min at 20 °C, the brown solution was evaporated to dryness. Extraction of the residue with pentane (25 mL) gave a brown solution and an off-white powder of NaI. The pale brown powder of **9** was obtained after filtration of the solution, evaporation to dryness, and drying under vacuum for 12 h at room temperature. Yield: 99.0 mg (87%). Anal. Calcd for $C_{18}H_{52}N_3ISi_6U$: C, 25.61; H, 6.21; N, 4.98; I, 15.03. Found: C, 25.41; H, 6.04; N, 4.91; I, 15.00. ^{1}H NMR (THF-d_8, 23 °C): δ 44.85 (s, 18 H, $SiMe_3$), 11.75 (s, 6 H, $SiMe_2$), 7.30 (s, 6 H, $SiMe_2$), −38.89 (s, 18 H, $SiMe_3$), −119.57 (s, 2 H, CH_2), −126.10 (s, 2 H, CH_2). ^{1}H NMR (THF-d_8, −107 °C): δ 105.15 (s, 9 H, $SiMe_3$), 101.77 (s, 9 H, $SiMe_3$), 31.31 (s, 3 H, $SiMe_2$), 14.27 (s, 3 H, $SiMe_2$), 10.45 (s, 6 H, $SiMe_2$), −66.95 (s, 18 H, $SiMe_3$), −138.77 (s, 1 H, CH_2), −181.48 (s, 1 H, CH_2), −373.45 (s, 1 H, CH_2), −493.22 (s, 1 H, CH_2).

Crystallography. The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[13] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to $\theta = 25.7°$ and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[14] Absorption effects were corrected empirically with the program SCALEPACK.[14] The structures were solved by direct methods (Patterson map interpretation for **5c** and **6**) with SHELXS-97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least-squares on F^2 with SHELXL-97.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the metallacycle

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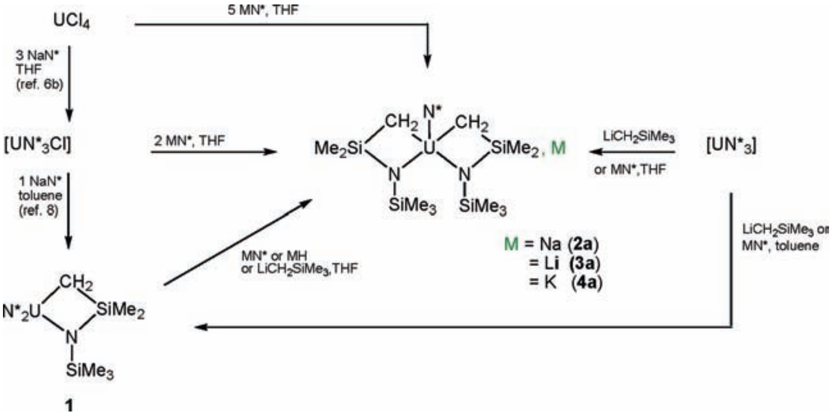
Scheme 1. Syntheses of the Complexes [MUN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]



methylene groups were found on Fourier-difference maps, and all the others were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Special details are as follows:

Compound 2a·1/6*n*-pentane. The solvent *n*-pentane molecule was given an occupancy factor of 0.5 (i.e., ~0.17 per uranium atom) to retain acceptable displacement parameters.

Compound 2d. The orthorhombic system can be ruled out since it corresponds to an internal *R* factor of 0.46. Restraints on some bond lengths and/or displacement parameters were applied for the atoms of the crown ether and THF moieties, the former being seemingly affected by unresolved disorder.

Compound 5c. The crown ether bound to Na2 is very badly resolved, probably because of disorder effects, and numerous restraints on bond lengths and displacement parameters (SIMU) had to be applied. Some voids in the lattice likely indicate the presence of unresolved solvent molecules.

Compound 8·0.5py. Because of the very low crystal and hence data quality, many restraints on bond lengths and displacement parameters had to be applied, particularly for the terminal methyl groups and the THF and pyridine molecules. The hydrogen atoms were not introduced in the disordered pyridine half molecule.

Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with SHELXTL.[15]

Results and Discussion

Synthesis and Crystal Structures of the Complexes Containing the Bis Metallacyclic Anion [UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$^-$. The uranium(IV) metallacycle [UN*$_2$($CH_2SiMe_2N\{SiMe_3\}$)] (**1**) was synthesized as previously described, by treating the chloride precursors [UN*$_3$Cl] or UCl_4 with respectively one or four mol equivalents of NaN* in toluene.[8] Reactions of **1** with 1 mol equivalent of a variety of bases such as MN*, MH (M = Na, K) or $LiCH_2SiMe_3$ in toluene were very slow, not being achieved after several weeks, whereas they rapidly went to completion in THF at 20 °C, within a few minutes or hours, to give after usual workup green powders of the anionic bismetallacycles [M(THF)$_x$UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$_n$ [M = Na (**2**), Li (**3**), or K (**4**)] resulting from γ metalation of a second amido ligand (Scheme 1). Expectedly, compound **2** was also obtained from [UN*$_3$Cl] or more directly from UCl_4 by treatment with NaN* in THF. The value of x was dependent on the drying conditions and satisfactory elemental analyses (C, H, N, Na) were obtained for the green powder of **2a** (x = 0), isolated with a 74% yield from UCl_4. Compounds **2**−**4** are highly air sensitive but have a good thermal stability in solution and the solid state. They are soluble in Et_2O, toluene and partially in pentane when containing THF ($x \geq 1$). The ^1H NMR spectra of **2**−**4** in THF-d_8, which are identical, exhibit two signals at δ 39.77 and −36.96, each integrating for 18 H and unequivocally assigned to the $SiMe_3$ groups, and four resonances at δ 32.18, −5.96, −286.20, and −297.80 in the area ratio of 6:6:2:2 corresponding to the non-equivalent methyl groups and methylene hydrogens of the cycles.

Complexes **2** and **3** were found to be formed by reaction of the uranium(III) trisamide [UN*$_3$] with NaN* or $LiCH_2SiMe_3$ in THF, in an attempt to synthesize the uranium(III) monometallacycles [M(THF)$_x$UN*$_2$($CH_2SiMe_2N\{SiMe_3\}$)] (M = Na, Li). It seems likely that the latter were oxidized into the bismetallacycles **2** and **3** following γ-CH activation and H_2 elimination. The same reactions in toluene afforded the uranium(IV) monometallacycle **1** (NMR experiments). In contrast, the uranium(III) bismetallacycle [Li(DME)U($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$_2$ was isolated from the reaction of [UN*$_2Cl_2$] and MeLi in DME;[5] its stability toward oxidation could be related to the absence of further possible γ-metalation of a N* ligand. It is interesting to note that the synthesis of the lanthanide compounds [Na(THF)$_x$LnN*$_2$($CH_2SiMe_2N\{SiMe_3\}$)] (Ln = Sc, Yb, Lu) from [LnN*$_3$] and NaN* was less easy than that of **2**,[3b] requiring 2 days in refluxing THF.

As summarized in Scheme 2, crystallization of **2** from pentane afforded green crystals of **2a**·1/6*n*-pentane (x = 0), **2b** (x = 1), or **2c** (x = 2), and crystallization in the presence of 18-crown-6 or 15-crown-5 gave green crystals of [Na(18-crown-6)(THF)][UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2d**) or [Na(15-crown-5)][UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2e**); these crystals were suitable for X-ray diffraction. After the zirconium complex [Zr($CH_2SiMe_2N\{SiMe_3\}$)$_2$(dmpe)][16] and the uranium(III) and uranium(V) compounds [Li(DME)U($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$_2$ and [UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$],[5] complexes **2a**−**2e** are new examples of such bis metallacycles to have been crystallographically characterized.

Views of the monomeric and simplest compounds **2d** and **2e** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 2. The uranium atoms are in a distorted trigonal bipyramidal environment with the two nitrogen atoms N(1) and N(2) of the metallacycles in axial positions. The geometrical parameters of the

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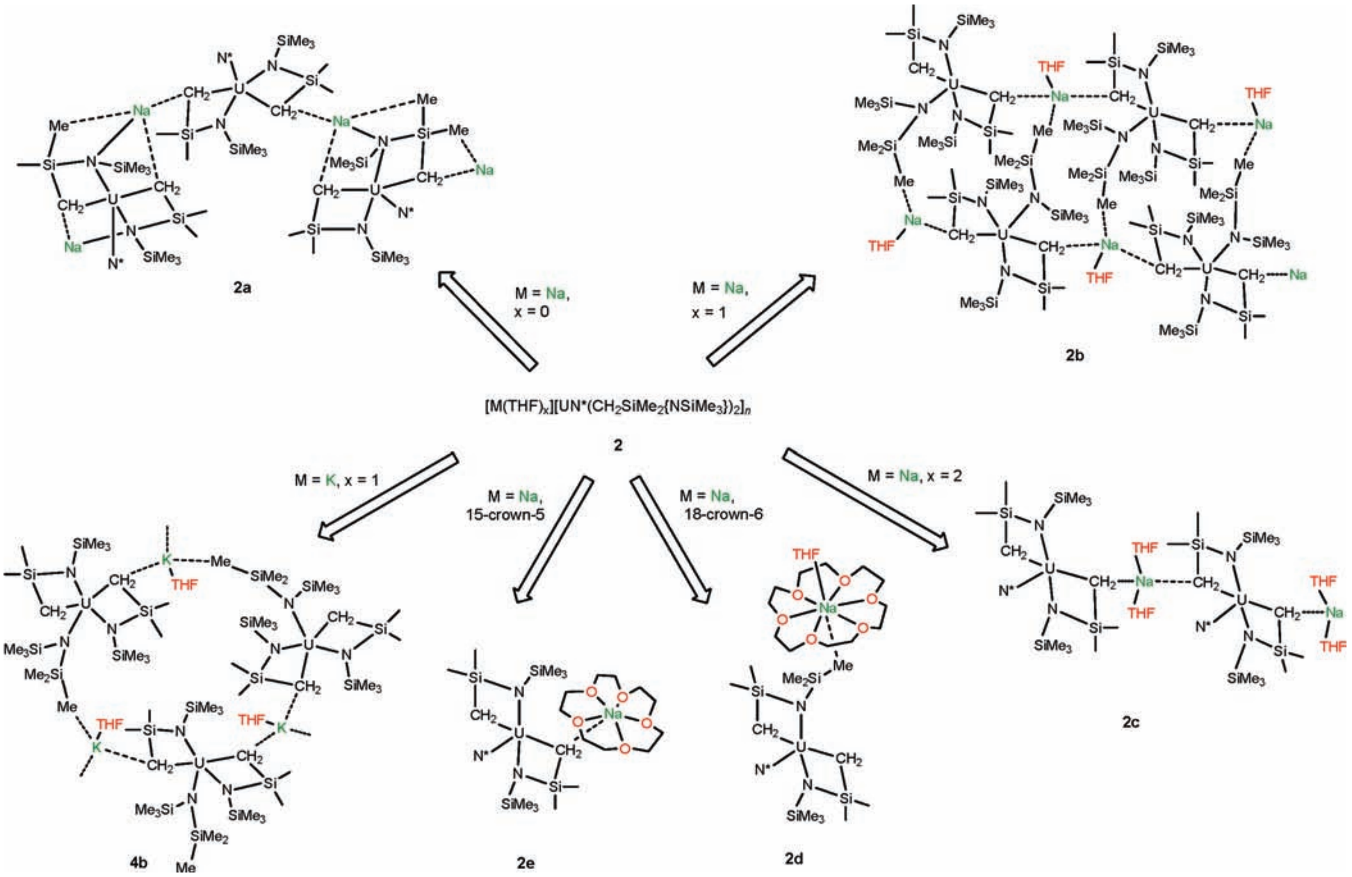
Scheme 2. Structures of the Complexes [M(L)UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] [L = (THF)$_x$ or crown ether]



U−N−Si−C cycles, which are planar [rms deviations of 0.005−0.048 Å] and form an interplanar angle of 75.60(10)° in **2d** and 75.47(14)° in **2e**, respectively, are similar to those determined in [U(CH$_2$SiMe$_2$N{SiMe$_3$})(Cp*)$_2$].[7u] The average U−C and U−N distances of 2.47(3) and 2.282(3) Å, respectively, and the average N−U−C angle of 70.5(3)° can be compared with the corresponding values of 2.52(2), 2.221(8) Å and 70.5(4)° in the aforementioned biscyclopentadienyl compound.[7u] The U−C1 bond in **2e** is about 0.05 Å longer than the other U−C bonds since C1 is in bridging position between the U and Na atoms. The average U−N3 distance of 2.357(1) Å is at the upper limit of the range of U−N bond lengths for terminally coordinated amide ligands (typically equal to 2.25 Å),[7g] being similar to those of 2.31(1)−2.44(1) Å in the anionic amido complex [Li(OEt$_2$)][U(NPh$_2$)$_3$(O)].[17] Complexes **2d** and **2e** form tight cation−anion pairs where the sodium atom is linked to one metallacycle via an agostic interaction with a methyl group of the NSiMe$_3$ fragment in **2d** or a methylene group in **2e**. The Na−C4 distance of 3.017(8) Å in **2d** and the Na−C1 distance of 2.744(6) Å in **2e** can be compared with those of 3.096(3) Å in [Na(THF)$_2$-(SiBu$^t_3$)],[18] 2.703(4)−3.469(6) Å in [NaZn(CH$_2$SiMe$_3$)$_3$][19] and 2.628(5) Å in [Na(THF)$_3$LnN*$_2$(CH$_2$SiMe$_2$N{SiMe$_3$})] (Ln = Sc, Yb).[3b,c] Such interactions determine the topology of the polymeric structures of **2a**−**2c**.

Views of compounds **2a**, **2b**, and **2c** are shown in Figures 3, 4, and 5, respectively, while selected bond lengths and angles are listed in Table 2. All the complexes are built of the same [UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] units which are linked together via Na atoms in bridging position between methylene groups of adjacent units. Thus are formed infinite chains ensured by U−CH$_2$−Na−CH$_2$−U linkages. The geometrical parameters of these units in **2a**−**2c** are quite similar to those in **2d** and **2e**; the U−C distances which average 2.51(2) Å are equal to the U−C1 bond length in **2e**. The Na−C distances which vary from 2.527(8) to 2.740(3) Å with an average value of 2.6(1) are smaller than the Na−C1 distance in **2e**, likely reflecting the lesser steric hindrance and electron richness of the Na atoms; these distances can be compared with those of 2.669(2) Å in [Na(TMEDA)(μ-Bu^n)(μ-TMP)Mg(TMP)] (TMPH = 2,2,6,6-tetramethylpiperidine)[20] or 2.515(6) and 2.544(6) Å in [Na$_2$Li$_2$(TMEDA)$_4$(μ-CH$_2$-Ph)$_4$].[21] The structure of **2b** exhibits two distinct chains with U−CH$_2$−Na−CH$_2$−U linkages running along the *a* axis, one with U1 and Na1 and the other with U2 and Na2 atoms; these two chains are attached to each other via agostic interactions between the Na1 atoms and a methyl group of a N(SiMe$_3$)$_2$ ligand (C26), so as to form ribbons which are further connected to one another by the agostic interaction between Na2 and C13″. The sodium atoms thus compensate for the loss of one coordinated THF molecule by passing from **2b** to **2a**. The Na1−C26 and Na2−C13″ distances of

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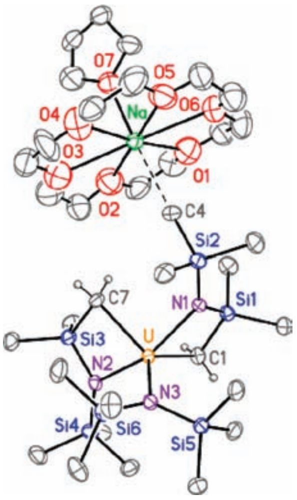

Figure 1. View of [Na(18-crown-6)(THF)][UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2d**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 30% probability level.

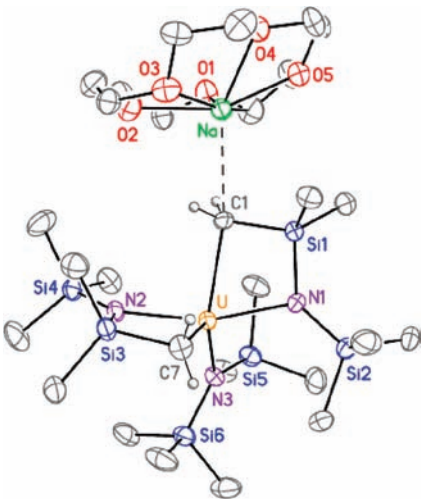

Figure 2. View of [Na(15-crown-5)][UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2e**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 30% probability level.

3.009(7) and 3.137(8) Å are similar to the Na−C4 distance in **2d**. In the structure of **2a**, the zigzag chains running along the *b* axis are composed of repeating motifs of three [UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] units which are linked by Na atoms in different ways. The Na2 and Na3 atoms join the central (U2) to the lateral units (U1 and U3) via the methylene group of one metallacycle, as in **2a** and **2b**, and are also attached to the other metallacycle of each lateral unit by the Na2−N1 or Na3−N7 bond and the Na2−C2 or Na3−C39 agostic interaction with one methyl group of the $SiMe_2$ fragment. The second methyl group (C38) of this $SiMe_2$ fragment of the lateral unit (U3) is involved in an agostic interaction with Na1 which is attached to the methylene group of the same metallacycle. The lateral units (U1 and U3′) are linked by Na1 via the Na1−N2 bond with the nitrogen atom of one metallacycle, in addition to the Na1−C1 bond with the methylene group of the other metallacycle.

Changing NaN* or NaH with the potassium analogues in their reaction with **1** led to the formation of the green powder of the solvent-free compound [KUN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$_n$ (**4a**) in 80% yield; green crystals of [K(THF)UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$_n$ (**4b**) were obtained by heating a suspension in pentane of a less thoroughly dried powder of **4**. A view of the asymmetric unit of **4b** is shown in Figure 6, and selected bond lengths and angles are listed in Table 2. The structure exhibits the same anionic uranium moiety as in compounds **2**, which is surrounded by three potassium atoms, two of these being linked to the methylene groups of the two metallacycles, as in **2**, and the third one exhibiting an agostic interaction with a methyl group of the $N(SiMe_3)_2$ fragment. Corrugated layers parallel to the *ab* plane are thus formed, which comprise chains of cyclic (U−N−Si−C−K−C)$_2$−U−C fragments in which the U, C, and K atoms are arranged in a helicoidal fashion along the *b* axis. The geometrical parameters of the metallacycles do not differ from those of compounds **2**. The K−C1 and K−C7′ distances of 3.003(5) and 3.048(6) Å can be compared with that of 3.101(7) Å in [K(PMDETA)(μ-Et)(μ-TMP)ZnEt] (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine),[22] and the K−C13″ distance of 3.243(6) Å can be compared with the average values of 3.19(4) Å in [$KZn(CH_2SiMe_3)_3$][19] or 3.33(5) Å in [{KSi{$SiMe_3$}$_3$}$_2$].[23]

Attempts at the synthesis of the dianionic trismetallacyclic complex [U($CH_2SiMe_2N\{SiMe_3\}$)$_3$]$^{2-}$ by γ C−H deprotonation of the last N* ligand of **2** were not conclusive. No reaction was observed with NaN* while mixtures of unidentified compounds were obtained by using methyl- or butyllithium. Reaction of **2** with $LiCH_2SiMe_3$ was cleaner, leading to the formation of a major product whose ^{1}H NMR spectrum exhibits three signals in the area ratio of 9:6:2 which would correspond to the equivalent metallacycles of the desired compound. However, this complex was found to be quite unstable and could not be separated from decomposition products.

Reactions of the Bis Metallacyclic Anion [UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]$^-$. Insertion of carbon monoxide into actinide−carbon or actinide−nitrogen bonds is well documented,[9a,24] and different products could be expected from the reaction of **2** and CO. The insertion into the U−N bonds was unlikely because of the presence of the electron withdrawing $SiMe_3$ substituent.[25] However, the outcome of the insertion reaction into the U−C bonds was not predictable in view of previous results since the monometallacycle **1** or the double tuck-in metallocene [U(η^5:η^1-C_5Me_4−$SiMe_2$-CH_2)$_2$] reacted with CO to give the five-membered ring enolate compounds [UN*$_2$(OC{=CH_2}$SiMe_2N\{SiMe_3\}$)][9a] or [U{η^5:η^1-C_5Me_4−$SiMe_2${=CH_2}CO}$_2$][26] with an exocyclic C=CH_2 double bond, whereas the bis alkyl compound [U(Cp*)$_2$(CH_2SiMe_3)$_2$] was converted into the enediolate derivative [U(Cp*)$_2$(OC{CH_2SiMe_3}=C{CH_2SiMe_3}O)] (Scheme 3).[19] These results were accounted for by the initial

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complexes [MUN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$]

	M = Na (**2a**)[a]		M = Na-(THF) (**2b**)[b]		M = Na-(THF)$_2$ (**2c**)[c]		M = Na(18-crown-6)-(THF) (**2d**)		M = Na-(15-crown-5) (**2e**)		M = K-(THF) (**4b**)[d]	
U−C	U1−C1	2.467(6)	U1−C1	2.532(6)	U−C1	2.518(3)	U−C1	2.457(6)	U−C1	2.505(6)	U−C1	2.532(4)
	U1−C7	2.506(6)	U1−C7	2.506(6)	U−C7	2.504(3)	U−C7	2.462(6)	U−C7	2.436(6)	U−C7	2.506(5)
	U2−C19	2.545(6)	U2−C23	2.522(6)								
	U2−C25	2.525(7)	U2−C29	2.532(6)								
	U3−C37	2.536(6)										
	U3−C43	2.480(6)										
U−N(cycle)	U1−N1	2.302(6)	U1−N1	2.271(6)	U−N1	2.265(2)	U−N1	2.283(5)	U−N1	2.278(5)	U−N1	2.279(4)
	U1−N2	2.313(5)	U1−N2	2.256(6)	U−N2	2.269(2)	U−N2	2.285(5)	U−N2	2.281(4)	U−N2	2.264(4)
	U2−N4	2.253(5)	U2−N4	2.278(5)								
	U2−N5	2.261(5)	U2−N5	2.269(5)								
	U3−N7	2.343(5)										
	U3−N8	2.230(5)										
U−N*	U1−N3	2.296(5)	U1−N3	2.359(5)	U−N3	2.347(2)	U−N3	2.358(5)	U−N3	2.356(5)	U−N3	2.332(4)
	U2−N6	2.295(6)	U2−N6	2.337(6)								
	U3−N9	2.318(5)										
Na−C or K−C	Na1−C1	2.616(8)	Na1−C1	2.655(7)	Na−C1	2.696(3)	Na−C4	3.017(8)	Na−C1	2.744(6)	K−C1	3.003(5)
	Na1−C8	3.051(7)	Na1−C7′	2.690(7)	Na−C7′	2.740(3)					K−C7′	3.048(6)
	Na1−C37′	2.616(6)	Na1−C26	3.009(7)							K−C13″	3.243(6)
	Na1−C38′	2.976(7)	Na2−C23	2.650(7)								
	Na2−C2	3.010(7)	Na2−C29′	2.652(7)								
	Na2−C7	2.621(8)	Na2−C13″	3.137(8)								
	Na2−C19	2.576(7)										
	Na3−C25	2.527(8)										
	Na3−C39	3.114(7)										
	Na3−C43	2.555(7)										
M−O or K−O			Na1−O1	2.291(6)	Na−O1	2.314(3)	Na−O7	2.344(7)	<Na−O-(crown)>	2.40(3)	K−O1	2.585(4)
			Na2−O2	2.316(6)	Na−O2	2.322(2)	<Na−O-(crown)>	2.74(7)				
N(cycle)−U−N(cycle)	N1−U1−N2	153.97(18)	N1−U1−N2	145.9(2)	N1−U−N2	148.37(9)	N1−U−N2	150.91(18)	N1−U−N2	153.48(17)	N1−U−N2	151.06(15)
	N4−U2−N5	149.76(19)	N4−U2−N5	145.2(2)								
	N7−U3−N8	150.22(19)										
C−U−N(cycle)	C1−U1−N1	71.9(2)	C1−U1−N1	69.9(2)	C1−U−N1	69.81(9)	C1−U−N1	70.81(19)	C1−U−N1	70.1(2)	C1−U−N1	70.53(14)
	C7−U1−N2	71.0(2)	C7−U1−N2	70.1(2)	C7−U−N2	70.19(9)	C7−U−N2	70.46(19)	C7−U−N2	70.8(2)	C7−U−N2	71.02(16)
	C19−U2−N4	70.24(19)	C23−U2−N4	69.3(2)								
	C25−U2−N5	70.1(2)	C29−U2−N5	69.8(2)								
	C37−U3−N7	70.06(18)										
	C43−U3−N8	72.12(19)										

[a] Symmetry code: ′ = $x, y - 1, z$. [b] Symmetry codes: ′ = $x + 1, y, z$; ″ = $x + 1, 1/2 - y, z - 1/2$. [c] Symmetry code: ′ = $x - 1, y, z$. [d] Symmetry codes: ′ = $-x, y + 1/2, 3/2 - z$; ″ = $1 - x, y + 1/2, 3/2 - z$.

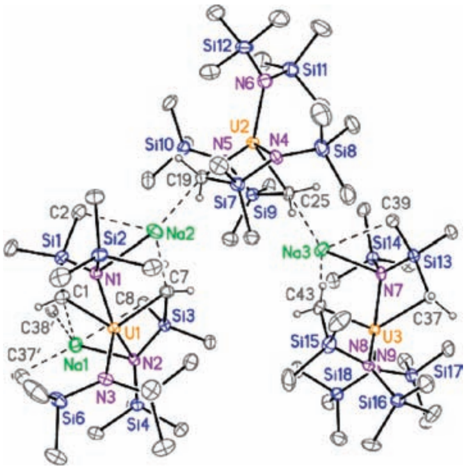


Figure 3. View of [NaUN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2a**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: $' = x, y - 1, z$.

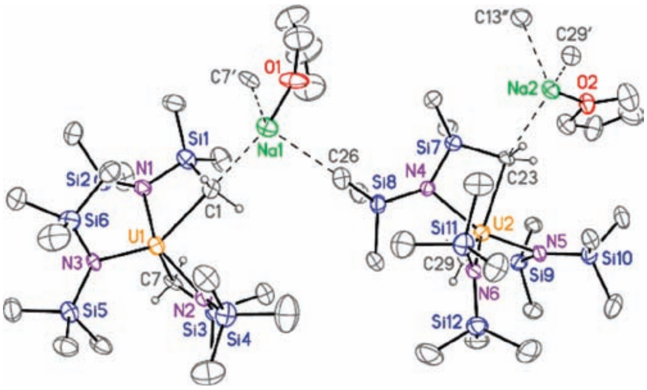


Figure 4. View of [Na(THF)UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2b**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes: $' = x + 1, y, z$; $'' = x + 1, 1/2 - y, z - 1/2$.

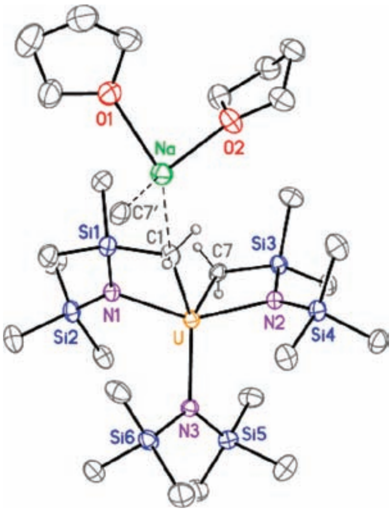


Figure 5. View of [Na(THF)$_2$UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**2c**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 40% probability level. Symmetry code: $' = x - 1, y, z$.

formation of dihapto acyl intermediates which can be described by the two resonance structures **A** and **B** in Scheme 3.

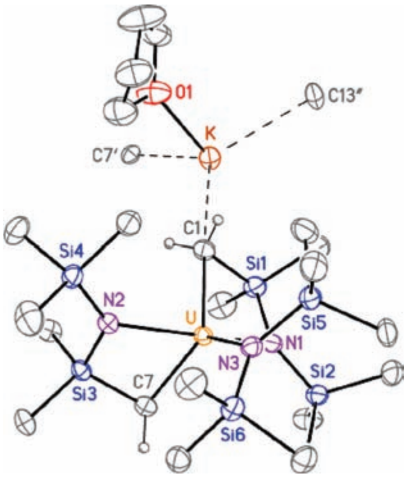


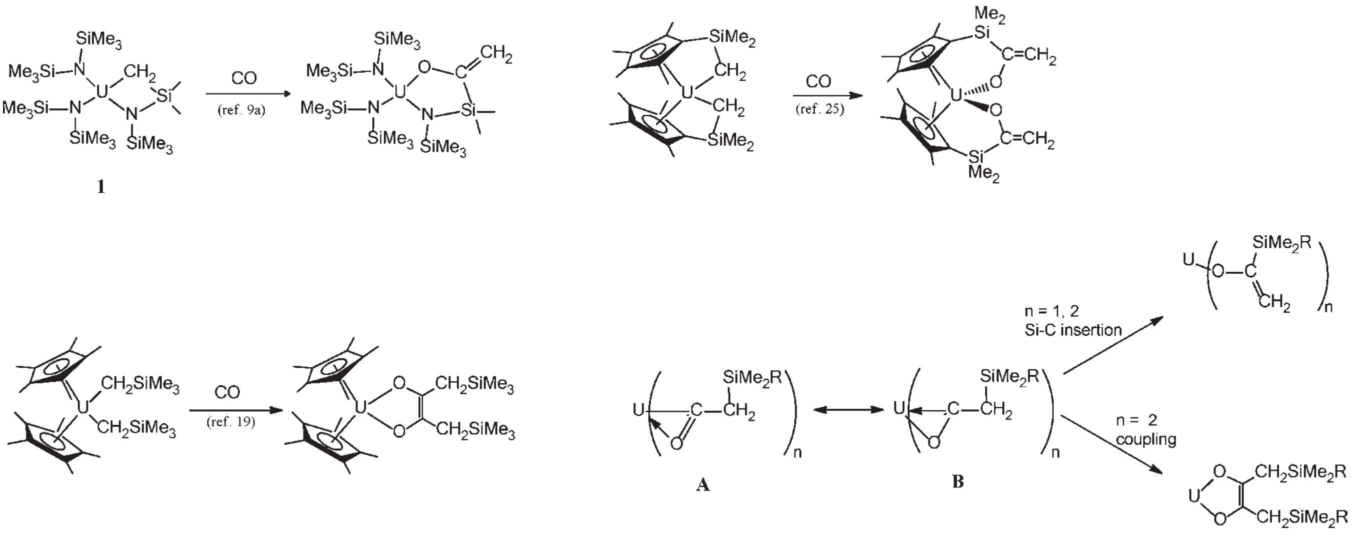
Figure 6. View of [K(THF)UN*($CH_2SiMe_2N\{SiMe_3\}$)$_2$] (**4b**). The hydrogen atoms are omitted except those of the metallacycle methylene groups. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: $' = -x, y + 1/2, 3/2 - z$; $'' = 1 - x, y + 1/2, 3/2 - z$.

Form **B** is likely to be responsible for the remarkable reactivity of the acyl group which reflects the carbene or carbenium ion character of the carbon atom. Rearrangement of the carbene-like species can proceed either by insertion into the weakest C$-$Si bond with formation of the exocyclic $C{=}CH_2$ bond or, in the case of a bis acyl intermediate from a bis alkyl precursor, by coupling into the enediolate product.

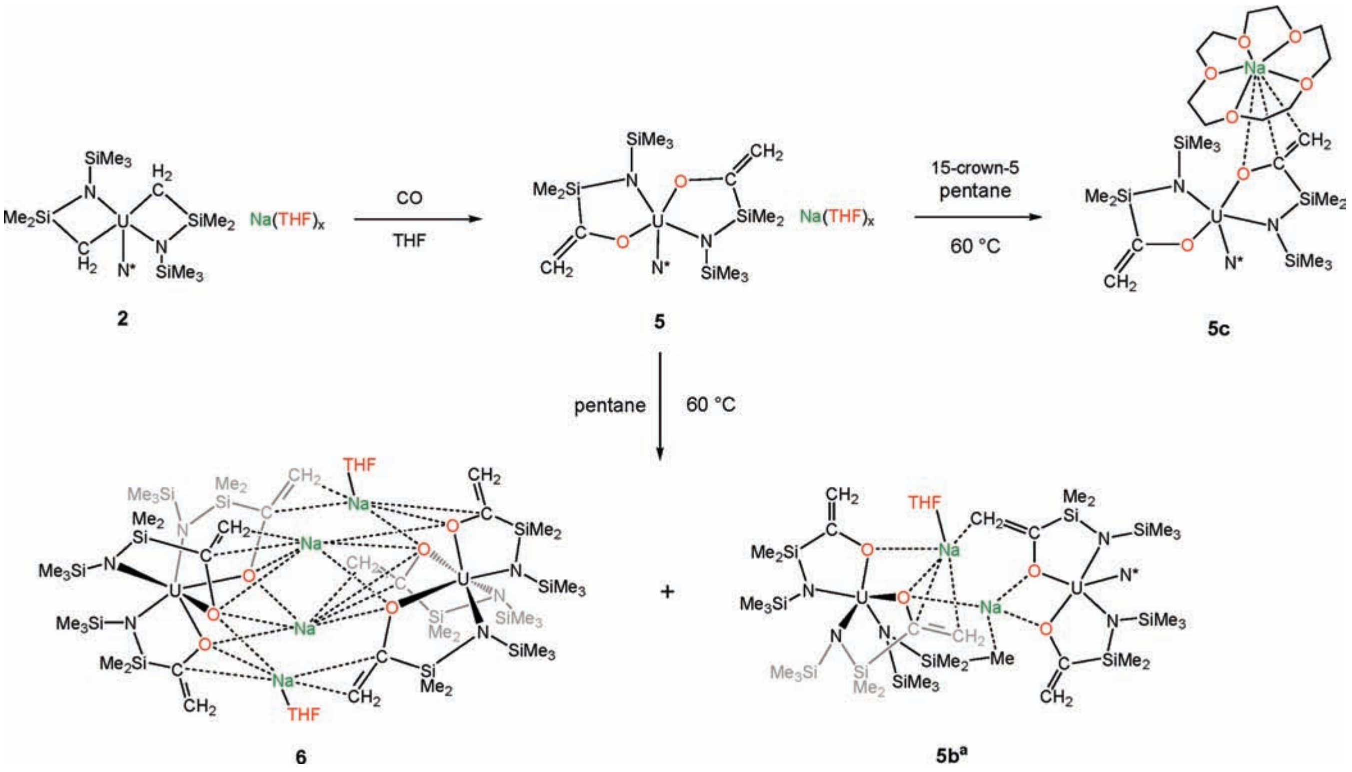
Diffusion of CO into a solution of **2** in THF-d_8 led immediately to the fading of the green color, and after 5 h, the ^{1}H NMR spectrum of the single product exhibited the same pattern of signals as **2**, with the intensity ratio of 18:18:6:6:2:2, but with the spectacular shift of the high field resonances of the methylene groups at δ $-$286.20 and $-$297.80 in **2** toward the low field region, at δ 85.27 and 54.00. After evaporation of the solvent, the green powder of the bis five-membered ring compound [Na(THF)$_x$UN*(OC{$=CH_2$}$SiMe_2N\{SiMe_3\}$)$_2$] (**5**) was isolated in almost quantitative yield; satisfactory elemental analyses were obtained for $x = 0$ (**5a**). The IR spectrum displays no frequency assignable to an acyl group resulting from the simple insertion of CO into the U$-$CH$_2$ bond but instead an absorption band at 1569 cm^{-1} which corresponds to the exo cyclic $C{=}CH_2$ bond of an enolate ligand, as found in [Zr(OC{$=CH_2$}$SiMe_2N\{SiMe_3\}$)$_2$($Me_2PCH_2CH_2PMe_2$)$_2$] (1568 cm^{-1})[16] and [U{η^5:η^1-$C_5Me_4-SiMe_2$\{$=CH_2$\}CO}$_2$] (1578 cm^{-1}).[26] The facile reaction of **2** with CO (1 atm) in a coordinating solvent is in striking contrast with that of **1** or its thorium derivative which, in toluene, slowly inserted CO under pressure (18 atm) whereas the methyl complex [UN*$_3$Me] was inert toward a high pressure of carbon monoxide.[9a,d] This distinct behavior may be accounted for by the greater nucleophilic character of the U$-$CH$_2$ bond of **2**.

Heating a suspension of the powder of **5** in pentane gave a mixture from which a few small green crystals of [Na$_2$(THF)-U$_2$N*$_2$(OC{$=CH_2$}$SiMe_2N\{SiMe_3\}$)$_4$] (**5b**) (Scheme 4) and many larger, well-shaped green crystals of the dianionic tris metallacyclic complex [Na$_2$(THF)U(OC{$=CH_2$}$SiMe_2N\{SiMe_3\}$)$_3$]$_2$ (**6**) could be separated. Formation of **6**, which is in fact the product of CO insertion into the putative tris metallacycle [Na$_2$(THF)$_x$U($CH_2SiMe_2N\{SiMe_3\}$)$_3$], obviously resulted from thermal decomposition of **5** and is not

Scheme 3. Different Products from CO Insertion into U−C Bonds



Scheme 4. Reaction of [Na(THF)$_x$UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (**2**) and CO[a]



[a] Crystals of **5b** were obtained in one experiment.

understood. The ^{1}H NMR spectra of **6** in THF-d_8 showed the presence of the equilibrating mixture of the *fac* and *mer* isomers of the compound of the type M(unsymmetrical bidentate ligand)$_3$; the equilibrium is completely shifted toward the formation of the *fac* isomer at 23 °C and of the *mer* isomer at −77 °C.[27] Green crystals of [Na(15-crown-5)][UN*(OC{=CH$_2$}SiMe$_2$N{SiMe$_3$})$_2$] (**5c**) were obtained upon addition of the crown ether to **5** in pentane, or by addition of CO into a pentane solution of **2** in the presence of 15-crown-5.

Views of **5b** and **5c** (one of the two independent and quite identical molecules) are shown in Figures 7 and 8, and selected bond lengths and angles are listed in Table 3. The uranium atoms are at the center of distorted trigonal bipyramids; in **5c**, the oxygen atoms O1 and O2 or O3 and O4 of the cycles are in apical positions whereas in **5b**, these positions are occupied by the oxygen O2 (O4) and the nitrogen N1 (N4) atoms of the two distinct cycles. The distances between the uranium and the nitrogen atoms of the metallacycles and of the N* ligands, which average respectively 2.305(10) and 2.34(3) Å in **5b** and 2.318(1) and 2.314(7) Å in **5c**, are not significantly different from those

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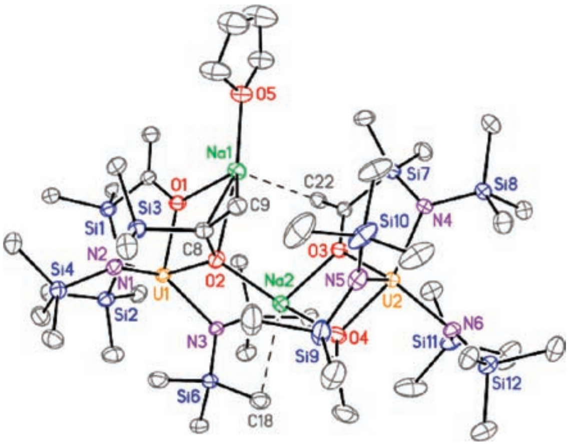

Figure 7. View of $[Na_2(THF)U_2N^*_2(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_4]$ (**5b**). The hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

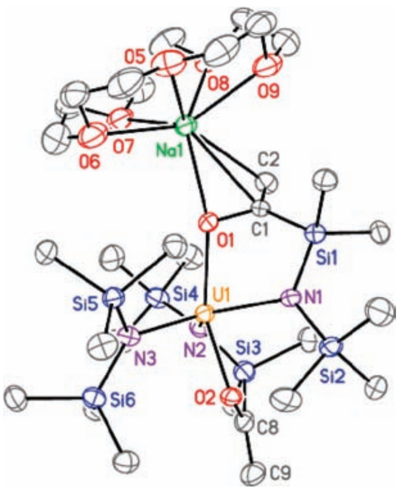

Figure 8. View of one of the two independent molecules in [Na(15-crown-5)UN*$(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_2$] (**5c**). The hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

measured in complexes **2** and **4**. The geometrical parameters of the enolate moieties are similar to those observed in [Na(12-crown-4)$_2$][TiN*$_2$$(OC\{=CH_2\}SiMe_2N\{SiMe_3\})$]^{28} and [VN*$(OC\{=CH_2\}SiMe_2N\{SiMe_3\})$]$_2$,^{29} the two other such metallacycles to have been crystallographically characterized; in particular, the average C−O and C−C distances of 1.384(14) and 1.327(7) Å in **5b** and 1.39(3) and 1.324(10) Å in **5c** can be compared with those of 1.36(1) Å in the titanium compound and 1.406(6) and 1.320(8) Å in the vanadium derivative where the oxygen atoms are in bridging positions. The structure of **5b** is built of two bis metallacyclic units which are linked by Na atoms in different fashions. The two oxygen atoms of each unit are bound to a sodium atom (O1 and O2 to Na1, O3 and O4 to Na2) which is attached to the other unit via the methylene group H_2C22 for Na1, and the oxygen O2 and the methyl group H_3C18 of the N* ligand in the case of Na2. The enolate fragments O2−C8−C9 in **5b** and O1−C1−C2 in **5c** are bound in a η^3 fashion to the Na1 atoms. The cationic Na(15-crown-5) fragment of **5c** is linked to the anionic UN*$(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_2$ unit via the oxygen atom O1 or O4 and the adjacent carbon−carbon double bond of one metallacycle. The Na1 atom in **5b** completes its coordination sphere with a THF molecule and the exocyclic C8═C9 bond. The U−O and Na−O distances, which average respectively 2.25(3) and 2.4(2) Å in **5b** and 2.20(5) and 2.50(4) Å in **5c**, can be compared with those of 2.29(1) and 2.47(1) Å in $[Na_2(THF)_6UO_2(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$.^{30} The U−O distance is larger than that of 2.132(2) Å measured in the double insertion product $[U(\eta^5{:}\eta^1\text{-}C_5Me_4{-}SiMe_2\{=CH_2\}CO)_2]$.^{26} The average Na1−C distance of 2.723(8) Å and the Na2−C18 distance of 2.930(5) Å in **5b**, and the mean Na−C bond length of 2.86(6) Å in **5c** are similar to those found in compounds **2**.

The centrosymmetric dimeric structure of **6** is shown in Figure 9, and selected bond lengths and angles are listed in Table 3. The uranium atom is at the center of a distorted *fac*-octahedron; the average U−O and U−N distances of 2.35(3) and 2.350(10) Å are about 0.05 Å larger than in **5**, reflecting the increase in coordination number. The sodium atoms Na1 and Na2 are attached to the tris metallacycle by O1 and O2 and by O2 and O3, respectively; the average Na−O distance of 2.38(7) Å is similar to that measured in **5**. Each sodium atom is linked to an exocyclic C═C bond of the symmetry-related tris metallacycle (⟨Na−C⟩ = 2.82(15) Å), ensuring the stability of the dimer. The O1−C1−C2 enolate fragment is η^3-coordinated to Na2. The $Na_4U_2O_6$ core of **6** is composed of two "open" heterocubane units which are fused by the Na2−O3−Na2′−O3′ face.

Compound **2** was converted in THF under an atmosphere of CO_2 into the insertion product $[Na(THF)_xUN^*(OC\{O\}CH_2SiMe_2N\{SiMe_3\})_2]$ (**7**) which precipitated and was isolated as a pale blue powder of **7a** (x = 0) in 60% yield after filtration and drying under vacuum; crystallization of **7** by diffusion of pentane into a pyridine solution afforded green crystals of $[Na(THF)_2(py)_2UN^*(OC\{O\}CH_2SiMe_2N\{SiMe_3\})_2]\cdot0.5py$ (**8**·0.5py) (Scheme 5). The NMR and IR spectroscopic data are consistent with insertion of CO_2 into the two U−C bonds. The ^1H NMR spectrum of **7** in pyridine-d_5 exhibits broad signals at 23 °C but is well resolved upon cooling the temperature below 0 °C, showing two sets of six resonances in the area ratio of 18:18:6:6:2:2 which indicate the presence of a 2:1 mixture of the two isomers in which the oxygen and nitrogen atoms of the metallacycles are in relative *cis* or *trans* positions. The IR spectrum exhibits frequencies assignable to the OC═O group at 1583 and 1623 cm^{-1}, which can be compared with those of 1540 and 1562 cm^{-1} in the indenyl and cyclopentadienyl compounds $[U(Ind^*)_2(O_2CMe)_2]^{10b}$ and $[U(C_5Me_4{-}SiMe_2CH_2CO_2)_2]$,^{31a} and 1615 cm^{-1} in the anionic bis(dimethylmalonato) uranyl complex $[UO_2(C_5H_6O_4)_2(H_2O)]^-$.^{31b} Compound **8** is the first crystallographically characterized complex resulting from CO_2 insertion into a $M(CH_2SiMe_2N\{SiMe_3\})$ metallacycle. Because of the lack of good quality crystals, the crystal structure of **8** could not be refined to a high accuracy, but it nevertheless establishes the connectivity unambiguously (Figure 10). The coordination geometry of the uranium atom is a quite perfect

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complexes $[Na_2(THF)U_2N^*_2(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_4]$ (**5b**), $[Na(15\text{-crown-}5)UN^*(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_2]$ (**5c**), and $[Na_2(THF)U(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_3]_2$ (**6**)

	5b		**5c**		6[a]	
U−N	U1−N1	2.288(3)	U1−N1	2.319(6)	U−N1	2.363(3)
	U1−N2	2.309(3)	U1−N2	2.320(6)	U−N2	2.349(3)
	U1−N3	2.372(3)	U1−N3	2.320(6)	U−N3	2.339(4)
	U2−N4	2.309(3)	U2−N4	2.316(6)		
	U2−N5	2.313(3)	U2−N5	2.319(6)		
	U2−N6	2.306(3)	U2−N6	2.307(6)		
U−O	U1−O1	2.220(3)	U1−O1	2.250(5)	U−O1	2.326(3)
	U1−O2	2.267(3)	U1−O2	2.154(5)	U−O2	2.342(3)
	U2−O3	2.286(3)	U2−O3	2.239(6)	U−O3	2.396(3)
	U2−O4	2.222(3)	U2−O4	2.153(5)		
Na−C	Na1−C8	2.728(4)	Na1−C1	2.803(8)	Na1−C8	3.122(5)
	Na1−C9	2.729(5)	Na1−C2	2.955(9)	Na1−C15′	3.015(5)
	Na1−C22	2.711(5)	Na2−C21	2.807(10)	Na1−C16′	2.667(6)
	Na2−C18	2.930(5)	Na2−C22	2.891(11)	Na2−C1′	2.685(5)
					Na2−C2′	2.905(6)
Na−O	Na1−O1	2.285(3)	Na1−O1	2.454(6)	Na1−O1	2.265(3)
	Na1−O2	2.780(3)	Na2−O3	2.537(7)	Na1−O2	2.422(4)
	Na1−O5	2.284(3)	⟨Na−O(crown)⟩	2.46(5)	Na1−O4	2.311(4)
	Na2−O2	2.273(3)			Na2−O1′	2.465(3)
	Na2−O3	2.313(3)			Na2−O2	2.295(3)
	Na2−O4	2.279(3)			Na2−O3	2.389(3)
					Na2−O3′	2.414(4)
N(cycle1)−U−O(cycle1)	N1−U1−O1	81.15(11)	N1−U1−O1	80.5(2)	N1−U−O1	79.32(11)
	N2−U1−O2	80.00(10)	N2−U1−O2	77.0(2)	N2−U−O2	77.21(11)
	N4−U2−O3	78.14(10)	N4−U2−O3	80.6(2)	N3−U−O3	81.38(12)
	N5−U2−O4	82.53(13)	N5−U2−O4	76.4(2)		
N(cycle1)−U−O(cycle2)	N1−U1−O2	157.35(11)	N1−U1−O2	85.9(2)	N1−U−O2	152.20(12)
	N2−U1−O1	96.53(11)	N2−U1−O1	94.1(2)	N1−U−O3	94.63(11)
	N4−U2−O4	151.12(11)	N4−U2−O4	86.2(2)	N2−U−O1	91.91(11)
	N5−U2−O3	109.49(11)	N5−U2−O3	94.4(2)	N2−U−O3	150.95(11)
					N3−U−O1	158.22(11)
					N3−U−O2	99.58(12)
O−U−O	O1−U1−O2	76.48(10)	O1−U1−O2	157.4(2)	O1−U−O2	73.47(10)
	O3−U2−O4	73.08(10)	O3−U2−O4	158.4(2)	O1−U−O3	76.87(11)
					O2−U−O3	73.93(10)

[a] Symmetry code: ′ = 2 − *x*, 1 − *y*, 1 − *z*.

trigonal bipyramid with the apexes occupied by the two oxygen atoms. Even though the oxygen atoms are not in bridging positions, the average U−O distance of 2.23 Å is similar to those found in **6**; these distances are smaller than in the U(IV) carboxylate compounds $[U(OC\{O\}CH_2OH)_4(H_2O)_2]$[32] (average 2.39(2) Å) or $[U(\{2,6\text{-}OCO\}_2C_5H_3N)_2(H_2O)_3]$[33] (average 2.35(4) Å) which have larger coordination numbers.

It is interesting to note that **5b**, **5c**, **6**, and **8** exhibit a mononuclear structure, despite the enlargement of their metallacyclic rings by one or two atoms by comparison with their precursors **2**−**4**, and did not undergo ring-opening reactions leading to the formation of polynuclear compounds bridged by CH_2SiMe_2N fragments. Such transformations were observed with the nitrido bimetallic complexes $[Na(DME)_2(TMEDA)][(\{R_2N)_2U\}_2(\mu\text{-}N)(CH_2SiMe_2NR)]$ and $[(\{R_2N\}_2U)_2(\mu\text{-}N)(CH_2SiMe_2NR)]$ (R = $SiMe_3$) resulting from deprotonation of a $SiMe_3$ group of $[UN^*_3]$ during its reaction with NaN_3,[7v] and the dinuclear tuck-in-tuck-over tuck-over dialkyl Tren complex obtained from deprotonation of a methyl group of the Tren ligand of $[U(Tren)_3I(THF)]$ (Tren = $N\{CH_2CH_2NSiMe_3\}_3$).[34]

Amido groups proved to be useful ligands for the stabilization of high valent uranium compounds, and anionic amide complexes of U(IV) were easily oxidized into the corresponding neutral U(V) derivatives.[7g,35] Complex **2** could thus be viewed as a valuable precursor of U(V) organometallic derivatives and in particular $[UN^*(CH_2SiMe_2N\{SiMe_3\})_2]$

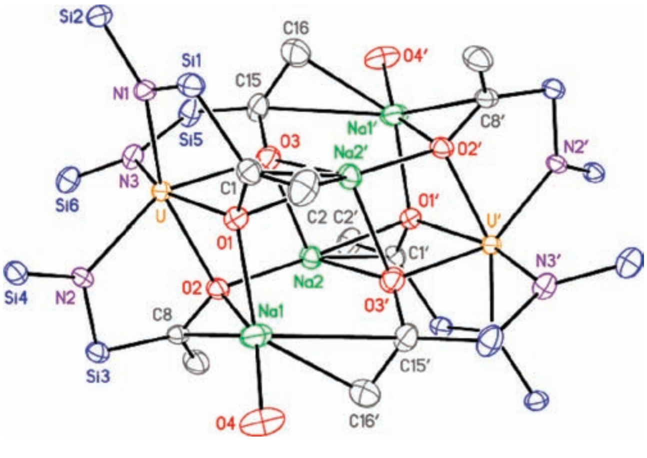

Figure 9. View of the dimeric structure of $[Na_2(THF)U(OC\{=CH_2\}SiMe_2N\{SiMe_3\})_3]_2$ (**6**). Hydrogen atoms and carbon atoms of methyl groups and THF ligands have been omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ′ = 2 − *x*, 1 − *y*, 1 − *z*.

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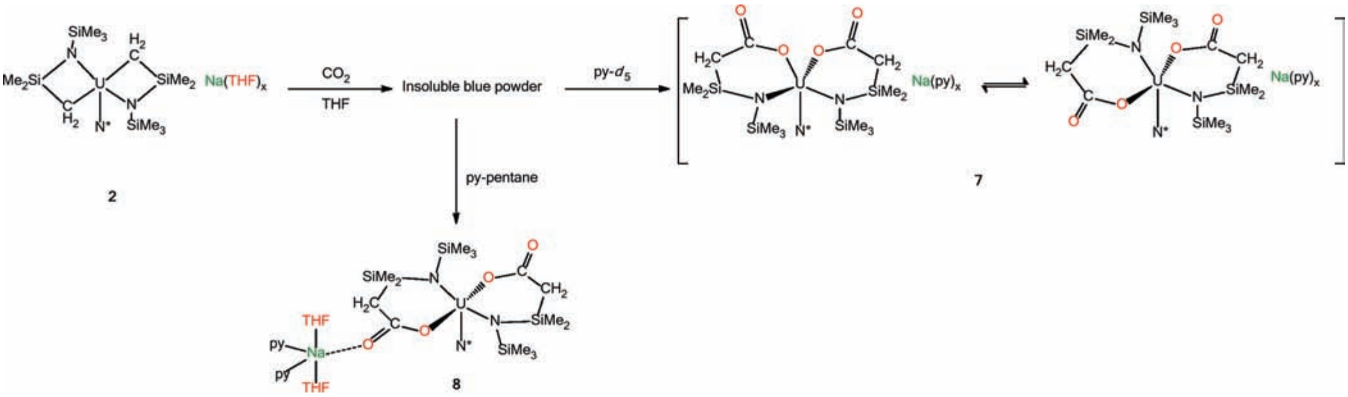
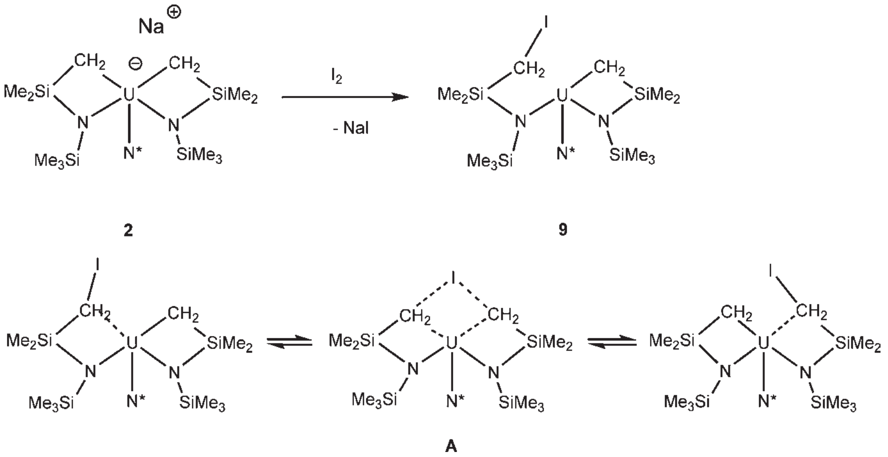
Scheme 5. Reaction of [Na(THF)$_x$UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (**2**) and CO$_2$



Scheme 6. Reaction of [Na(THF)$_x$UN*(CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (**2**) and I$_2$



which has been recently isolated from the reaction of [UN*$_2$Cl$_2$] with BuLi.[5] Our attempts at the synthesis of this U(V) complex by oxidation of **2** with TlBPh$_4$, AgI, CuCl, and O$_2$ were so far inconclusive, giving mixtures of unidentified products. The possible formation of the uranium(V) complex could not be demonstrated; no crystals suitable for X-ray diffraction were obtained while NMR spectra did not show any broad signals characteristic of a U(V) product.[5]

Treatment of **2a** with one mol equivalent of iodine in THF led to the cleavage of one U−C bond[36] and formation, after precipitation of NaI in pentane, of the neutral compound [UN*(CH$_2$SiMe$_2$N{SiMe$_3$})(N{SiMe$_3$}SiMe$_2$-CH$_2$I)] (**9**) which was isolated as a pale brown powder in 87% yield (Scheme 6).

The dissymmetric structure of **9** was demonstrated by the ^{1}H NMR spectrum in THF-d_8 at −107 °C which exhibited four signals at δ −138.77, −181.48, −373.45, and −493.22, each integrating for 1 H, corresponding to the four distinct hydrogens of the CH$_2$I and UCH$_2$ groups, and three signals of relative intensities 9:9:18 at δ 105.15, 101.77, and −66.95, assigned to the two NSiMe$_3$ and unique N(SiMe$_3$)$_2$ fragments. Coalescence of these signals occurred around −70 °C and in the fast limit spectrum at 23 °C, the CH$_2$ and SiMe$_3$ groups gave rise to four signals of relative intensities 2:2:18:18, characteristic of a symmetrical structure. These features can be interpreted by the equilibrium represented in Scheme 6 that is a degenerate σ bond metathesis reaction of U−C and C−I bonds which would involve the symmetrical four center transition state **A**. Complex **9** would thus represent a new

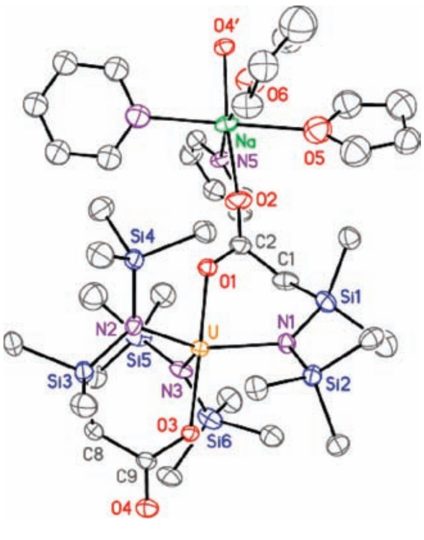


Figure 10. View of [Na(THF)$_2$(py)$_2$UN*(OC{O}CH$_2$SiMe$_2$N{SiMe$_3$})$_2$] (**8**). Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level. Symmetry code: ′ = $x + 1/2$, $1/2 - y$, $z - 1/2$.

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type of so-called "pendulum" systems,[37] typical examples of which were provided by the "bridge flipping" of 7-norbornadienyl cations,[37a,b] and the degenerate rearrangement of sulfonium ions modeling a permanent associative SN2 reaction at tetrahedral carbon.[37c] From line shape analysis of the spectra, the activation energy for the rearrangement of **9** is 7.5(1) kcal mol^{-1}. This low value is similar to that calculated for some 7-norbornadienyl cations.[37b]

Conclusion

Novel and rare examples of bis metallacyclic compounds of general formula $[ML_xUN^*(CH_2SiMe_2N\{SiMe_3\})_2]$ were isolated from γ-CH deprotonation reactions of $[UN^*_3Cl]$ or $[UN^*_2(CH_2SiMe_2N\{SiMe_3\})]$. These complexes, interesting for further reactivity studies, exhibit a variety of crystal structures depending on the nature of ML_x (M = Li, Na, or K and L = THF or crown ether) in which the $UN^*(CH_2SiMe_2N\{SiMe_3\})_2$ units are linked via CH_2 and/or CH_3 groups to Na or K atoms to give tight cation−anion pairs or 1D or 2D coordination polymers. The two U−C bonds, which are much more reactive than that in the $[UN^*_2(CH_2SiMe_2N\{SiMe_3\})]$ parent, readily inserted CO and CO_2 molecules, and a $M(OC\{O\}CH_2SiMe_2N\{SiMe_3\})$ metallacycle was crystallographically characterized for the first time. Treatment of the bis metallacyclic anion with iodine did not afford the corresponding neutral U(V) neutral compound, but led to the cleavage of one U−C bond and formation of a complex which would represent a new type of so-called "pendulum" systems resulting from a degenerate σ bond metathesis reaction of U−C and C−I bonds. Further reactions of these complexes, in particular the oxidation of the anionic species into uranium(V) derivatives, are currently studied.

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Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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