Iodide, Azide, and Cyanide Complexes of (N,C), (N,N), and (N,O) Metallacycles of Tetra- and Pentavalent Uranium

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Ⓢ *Supporting Information*

ABSTRACT: In contrast to the neutral macrocycle $[UN^*_2(N,C)]$ (**1**) $[N^* = N(SiMe_3)_3; N,C = CH_2SiMe_2N-(SiMe_3)]$ which was quite inert toward I_2, the anionic bismetallacycle $[NaUN^*(N,C)_2]$ (**2**) was readily transformed into the enlarged monometallacycle $[UN^*(N,N)I]$ (**4**) $[N,N = (Me_3Si)NSiMe_2CH_2CH_2SiMe_2N(SiMe_3)]$ resulting from C—C coupling of the two CH_2 groups, and $[NaUN^*(N,O)_2]$ (**3**) $[N,O = OC(=CH_2)SiMe_2N(SiMe_3)]$, which is devoid of any U—C bond, was oxidized into the U^V bismetallacycle $[Na\{UN^*(N,O)_2\}_2(\mu\text{-}I)]$ (**5**). Sodium amalgam reduction of **4** gave the U^{III} compound $[UN^*(N,N)]$ (**6**). Addition of MN_3 or MCN to the (N,C), (N,N), and (N,O) metallacycles **1**, **4**, and **5** led to the formation of the anionic azide or cyanide derivatives $M[UN^*_2(N,C)(N_3)]$ [M = Na, **7a** or Na(15-crown-5), **7b**], $M[UN^*_2(N,C)(CN)]$ [M = NEt$_4$, **8a** or Na(15-crown-5), **8b** or K(18-crown-6), **8c**], $M[UN^*(N,N)(N_3)_2]$ [M = Na, **9a** or Na(THF)$_4$, **9b**], $[NEt_4][UN^*(N,N)(CN)_2]$ (**10**), $M[UN^*(N,O)_2(N_3)]$ [M = Na, **11a** or Na(15-crown-5), **11b**], $M[UN^*(N,O)_2(CN)]$ [M = NEt$_4$, **12a** or Na(15-crown-5), **12b**]. In the presence of excess iodine in THF, the cyanide **12a** was converted back into the iodide **5**, while the azide **11a** was transformed into the neutral U^V complex $[U(N\{SiMe_3\}-SiMe_2C\{CHI\}O)_2I(THF)]$ (**13**). The X-ray crystal structures of **4**, **7b**, **8a−c**, **9b**, **10**, **12b**, and **13** were determined.
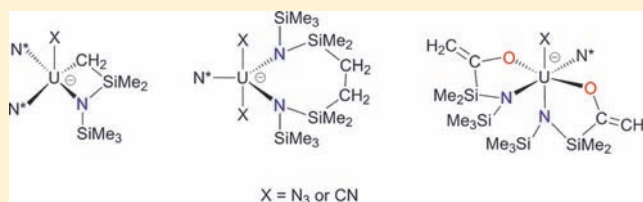
INTRODUCTION

The bis(trimethylsilyl)amide ligand (N* = N(SiMe$_3$)$_2$) has gained a prominent position in coordination chemistry mainly because of its remarkable capacity to stabilize metal centers in their lowest and highest oxidation states and its easy substitution with proton acidic molecules, affording a convenient synthetic route to a variety of inorganic and organometallic derivatives or active species in catalytic cycles.[1] The N* ligand can also undergo facile γ-CH deprotonation in basic medium and/or upon heating conditions, leading to the formation of the metallacycle $[M(\kappa^2(N,C)\text{-}CH_2SiMe_2N-\{SiMe_3\})]$, hereafter called $[M(N,C)]$.[2] Such a metallacycle was introduced by the groups of Andersen and Dormond in actinide chemistry with the uranium(IV) compound $[UN^*_2(N,C)]$ (**1**), formed by elimination of methane or hydrogen chloride from $[UN^*_3Me]$ or $[UN^*_3Cl]$, respectively.[3,4] Compound **1** exhibited a rich organometallic chemistry, including nucleophilic behavior toward carbonyl molecules and insertion reactions into the U−C bond, which was developed in the 1980s.[5] We found recently that **1** could be readily transformed into novel and rare examples of bis metallacyclic compounds of general formula $[ML_xUN^*(N,C)_2]$ (M = Li, Na or K and L = THF or crown ether) resulting from γ-metalation of a second N* ligand (Scheme 1).[6] Treatment of $[NaUN^*(N,C)_2]$ (**2**) with CO and CO$_2$ afforded the U−C bonds insertion products $[NaUN^*(\kappa^2(N,O)-OC\{=CH_2\}-SiMe_2N\{SiMe_3\})_2]$, hereafter called $[NaUN^*(N,O)_2]$ (**3**), and $[NaUN^*(\kappa^2(N,O)-OC\{O\}CH_2SiMe_2N\{SiMe_3\})_2]$, respectively. We further investigated the reactivity of **2** and **3**, with

a special attention to their potential as precursors of U^V and U^{VI} compounds, considering that their anionic character would favor their ready one electron oxidation and the presence of amide and alkoxide ligands would stabilize the high metal oxidation states. By comparison with complexes in the +3 and +4 oxidation state and with exception of uranyl derivatives, high-valent uranium compounds are rather uncommon, even though recent advances toward their synthesis have induced better knowledge of their physicochemical properties.[7] In view of their further oxidation and reactivity studies, we also prepared anionic complexes by addition of azide and cyanide ligands to the uranium(IV) metallacycles **1** and $[UN^*(N,N)I]$ (**4**) $[N,N = (Me_3Si)NSiMe_2CH_2CH_2SiMe_2N(SiMe_3)]$ and the uranium(V) derivative $[Na\{UN^*(N,O)_2\}_2(\mu\text{-}I)]$ (**5**), these two latter resulting from reaction of I_2 with **2** and **3**, respectively (Scheme 1). The choice of the N_3^- and CN^- ions was motivated by recent studies which revealed that both ligands strongly bind the metal center in different oxidation states and adopt several ligation modes, thus affording a variety of mono- and polynuclear complexes with novel structures, reactivity patterns, and physicochemical properties.[8,9] Furthermore, uranium azides are considered as precursors of imido and nitrido derivatives. Here we present the syntheses and X-ray crystal structures of these iodide, cyanide, and azide derivatives of U^{IV} and U^V (N,C), (N,O), and (N,N) metallacycles. Part of this work was presented in our preliminary communication.[10]

Scheme 1. Synthesis of the Complexes[a]
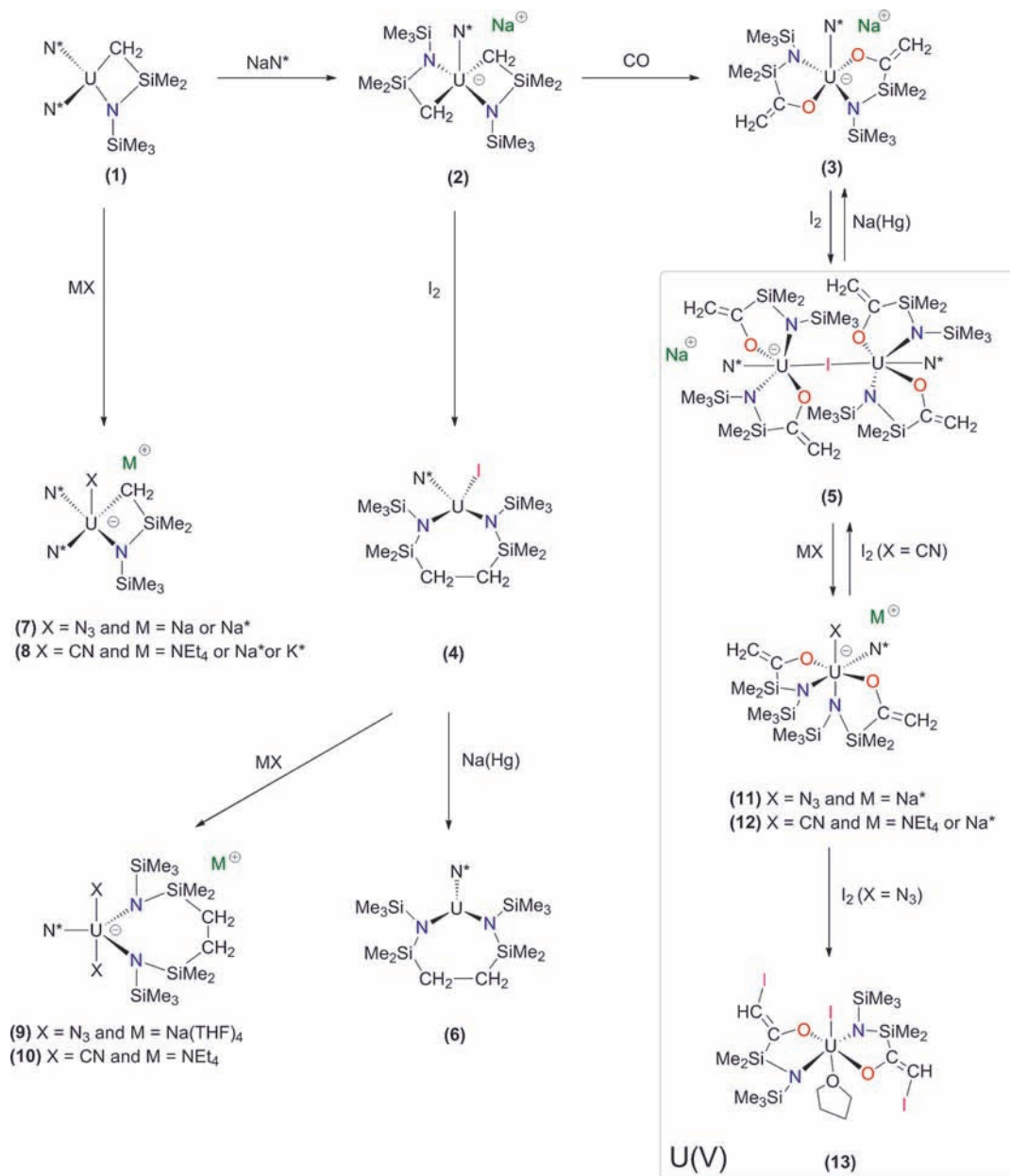
[a]Na* = Na(15-crown-5); K* = K(18-crown-6). All reactions are in THF except the syntheses of Na*[UN*$_2$(N,C)(N$_3$)] (**7b**), Na*[UN*(N,O)$_2$(N$_3$)] (**11b**), and Na*[UN*(N,O)$_2$(CN)] (**12b**) in pentane.

■ EXPERIMENTAL SECTION

General Information. 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 deuteriated 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). I$_2$, NaCN, NEt$_4$CN, and NaN$_3$ (Aldrich) were used without purification; 18-crown-6 and 15-crown-5 (Fluka) were dried under vacuum before use. The compounds [UN*$_2$(N,C)] (**1**),[4] [NaUN*(N,C)$_2$] (**2**),[6] and [NaUN*(N,O)$_2$] (**3**)[6] were synthesized as previously reported.

Synthesis of [UN*(N,N)I] (4). Complex **4** was previously incorrectly formulated as the isomer [UN*(N,C)(N{SiMe$_3$}-SiMe$_2$CH$_2$I)][6] and its synthesis is presented again here for a comprehensive report. A flask was charged with **2** (100 mg, 0.135 mmol) and I$_2$ (34.0 mg, 0.135 mmol), and THF (15 mL) was condensed in. 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 **4** 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$_3$ISi$_6$U: 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, $w_{1/2}$ = 130 Hz, CH$_2$), −126.10 (s, 2 H, $w_{1/2}$ = 180 Hz, CH$_2$). ^{1}H NMR (THF-d_8, −107 °C): δ 105.1 (s, 9 H, $w_{1/2}$ = 600 Hz, SiMe$_3$), 101.77 (s, 9 H, $w_{1/2}$ = 260 Hz, SiMe$_3$), 31.31 (s, 3 H, $w_{1/2}$ = 200 Hz,

Table 1. Crystal Data and Structure Refinement Details

	7b	8a	8b	8c
chemical formula	$C_{28}H_{73}N_6NaO_5Si_6U$	$C_{27}H_{73}N_5Si_6U$	$C_{29}H_{73}N_4NaO_5Si_6U$	$C_{31}H_{77}KN_4O_6Si_6U$
M (g mol^{-1})	1003.48	874.47	987.47	1047.64
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	12.1873(5)	12.2001(2)	11.2257(10)	12.9150(10)
b (Å)	21.4852(4)	21.9513(7)	13.1157(15)	22.1689(14)
c (Å)	18.4647(7)	16.3996(6)	17.7212(16)	17.7881(8)
α (deg)	90	90	92.207(6)	90
β (deg)	91.222(2)	95.847(2)	92.650(6)	91.926(4)
γ (deg)	90	90	111.385(5)	90
V (Å^3)	4833.8(3)	4369.1(2)	2422.6(4)	5090.1(6)
Z	4	4	2	4
D_{calcd} (g cm^{-3})	1.379	1.329	1.354	1.367
μ(MoKα) (mm^{-1})	3.552	3.901	3.541	3.449
$F(000)$	2040	1784	1004	2136
reflns collcd	141825	110712	105717	147447
indep reflns	9157	8282	9183	9611
obd reflns [$I > 2\sigma(I)$]	6728	6899	7278	5807
R_{int}	0.023	0.027	0.059	0.051
params refined	534	497	432	621
R1	0.053	0.029	0.048	0.084
wR2	0.163	0.072	0.131	0.253
S	1.052	1.120	1.037	1.016
$\Delta\rho_{min}$ (e Å^{-3})	−1.31	−0.85	−1.55	−1.25
$\Delta\rho_{max}$ (e Å^{-3})	1.47	0.62	1.55	5.31

	9b	10	12b	12b·0.5n-pentane
chemical formula	$C_{34}H_{84}N_9NaO_4Si_6U$	$C_{28}H_{72}N_6Si_6U$	$C_{31}H_{72}N_4NaO_7Si_6U$	$C_{33.5}H_{78}N_4NaO_7Si_6U$
M (g mol^{-1})	1112.66	899.49	1042.49	1078.56
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$C2/c$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a (Å)	18.9735(14)	11.4736(2)	14.5599(6)	16.9706(8)
b (Å)	11.9302(12)	17.1928(7)	20.6975(11)	17.0986(9)
c (Å)	25.002(3)	21.9491(9)	17.0668(6)	20.2357(7)
α (deg)	90	90	90	104.780(3)
β (deg)	104.028(6)	90	99.974(3)	90.054(3)
γ (deg)	90	90	90	100.926(2)
V (Å^3)	5490.6(10)	4329.8(3)	5065.4(4)	5567.1(4)
Z	4	4	4	4
D_{calcd} (g cm^{-3})	1.346	1.380	1.367	1.287
μ(MoKα) (mm^{-1})	3.134	3.940	3.394	3.091
$F(000)$	2280	1832	2116	2200
reflns collcd	54338	90907	240902	226173
indep reflns	5199	8190	9611	21095
obd reflns [$I > 2\sigma(I)$]	4051	7410	7627	15649
R_{int}	0.052	0.034	0.026	0.033
params refined	269	391	467	1027
R1	0.044	0.036	0.051	0.049
wR2	0.089	0.088	0.149	0.145
S	1.050	1.017	1.043	1.059
$\Delta\rho_{min}$ (e Å^{-3})	−1.12	−0.71	−0.93	−1.05
$\Delta\rho_{max}$ (e Å^{-3})	0.71	1.05	1.78	1.79

SiMe$_2$), 14.27 (s, 3 H, $w_{1/2}$ = 180 Hz, SiMe$_2$), 10.45 (s, 6 H, $w_{1/2}$ = 220 Hz, SiMe$_2$), −66.95 (s, 18 H, $w_{1/2}$ = 340 Hz, SiMe$_3$), −138.77 (s, 1 H, $w_{1/2}$ = 200 Hz, CH$_2$), −181.48 (s, 1 H, $w_{1/2}$ = 240 Hz, CH$_2$), −373.45 (s, 1 H, $w_{1/2}$ = 400 Hz, CH$_2$), −493.2 (s, 1 H, $w_{1/2}$ = 920 Hz, CH$_2$).

Reaction of 2 with C$_2$Cl$_6$. An NMR tube was charged with **2** (10.0 mg, 13.5 μmol) and C$_2$Cl$_6$ (3.2. mg, 13.5 μmol), and THF (2 mL) was condensed in. The reaction mixture was stirred for 20 min at 20 °C, and the brown solution was evaporated to dryness. Extraction of the residue with pentane (3 mL) gave a brown solution which was

filtered and evaporated to dryness, giving a pale brown powder which, in view of the ^{1}H NMR spectrum, would be the chloro analogue of **4**. ^{1}H NMR (THF-d_8, 23 °C): δ 32.27 (s, 18 H, SiMe$_3$), 9.20 (s, 6 H, SiMe$_2$), 7.58 (s, 6 H, SiMe$_2$), −30.86 (s, 18 H, SiMe$_3$), −100.40 (s, 2 H, CH$_2$), −108.86 (s, 2 H, CH$_2$).

Synthesis of [Na{UN*(N,O)$_2$}$_2$(μ-I)] (5). A flask was charged with **3** (221 mg, 277 μmol) and I$_2$ (35.8 mg, 141 μmol) in THF (15 mL). After 2 h at 20 °C, the solvent was evaporated off. The dark red residue was extracted in pentane (20 mL), and the dark red glass of **5**

was isolated after evaporation to dryness. Yield: 190 mg (81%). Anal. calcd for $C_{40}H_{104}IN_6NaO_4Si_{12}U_2$: C, 28.32; H, 6.18; N, 4.95. Found: C, 28.09; H, 5.89; N, 5.15. ^{1}H NMR (THF-d_8, 23 °C): δ 15.49 (s, $w_{1/2}$ = 95 Hz, 2 H, CH$_2$), 9.77 (s, $w_{1/2}$ = 110 Hz, 2 H, CH$_2$), 5.75 (s, $w_{1/2}$ = 75 Hz, 6 H, SiMe$_2$), 3.00 (s, $w_{1/2}$ = 43 Hz, 6 H, SiMe$_2$), −1.76 (s, $w_{1/2}$ = 65 Hz, 18 H, SiMe$_3$), −4.18 (s, $w_{1/2}$ = 48 Hz, 18 H, SiMe$_3$). IR (Nujol): ν/cm^{-1} 1590 w (C=CH$_2$).

Reduction of 5 with Sodium Amalgam. An NMR tube was charged with **5** (17.0 mg, 10 μmol) and 2% Na(Hg) (23 mg, 20 μmol) in THF-d_8 (0.5 mL). After stirring for 24 h at 20 °C, the spectrum showed the complete formation of **3**.

Synthesis of [UN*(N,N)] (6). A flask was charged with **4** (150 mg, 177 μmol) and 2% Na(Hg) (307 mg, 267 μmol), and THF (6 mL) was condensed in. After stirring for 24 h at 20 °C, the very dark purple reaction mixture was evaporated to dryness, leaving a dark purple powder. Extraction in pentane (8 mL) and evaporation to dryness afforded a very dark purple glass of **6** which was dried under vacuum for 15 h at 20 °C. Yield: 126 mg (99%). Anal. calcd for $C_{18}H_{52}N_3Si_6U$: C, 30.15; H, 7.31; N, 5.86. Found: C, 30.09; H, 7.04; N, 5.77. ^{1}H NMR (THF-d_8, 23 °C): δ 11.29 (s, $w_{1/2}$ = 32 Hz, 18 H, SiMe$_3$), 4.42 (s, $w_{1/2}$ = 39 Hz, 12 H, SiMe$_2$), −26.12 (s, $w_{1/2}$ = 38 Hz, 18 H, SiMe$_3$), −52.6 (s, $w_{1/2}$ = 310 Hz, 4 H, CH$_2$). ^{1}H NMR (THF-d_8, −107 °C): δ 38.4 (s, $w_{1/2}$ = 460 Hz, 18 H, SiMe$_3$), 4.5 (s, $w_{1/2}$ = 820 Hz, 12 H, SiMe$_2$), −31 (s, $w_{1/2}$ = 2200 Hz, 18 H, SiMe$_3$), −117.8 (s, $w_{1/2}$ = 430 Hz, 4 H, CH$_2$).

Synthesis of Na[UN*$_2$(N,C)(N$_3$)] (7a) and Crystals of [Na(15-crown-5)][UN*$_2$(N,C)(N$_3$)] (7b). (a) A flask was charged with **1** (100 mg, 139 μmol) and NaN$_3$ (10.9 mg, 167 μmol), and THF (10 mL) was condensed in. After stirring for 2 d at 20 °C, the solution was filtered and evaporated to dryness, leaving a brown powder of **7a**. Yield: 107 mg (98%). Anal. calcd for $C_{18}H_{53}N_6NaSi_6U$: C, 27.60; H, 6.82; N, 10.73. Found: C, 27.12; H, 6.55; N, 10.43. ^{1}H NMR (THF-d_8, 23 °C): δ 19.14 (s, $w_{1/2}$ = 8 Hz, 9 H, SiMe$_3$), 4.37 (s, $w_{1/2}$ = 6 Hz, 6 H, SiMe$_2$), −11.08 (s, $w_{1/2}$ = 12 Hz, 36 H, N(SiMe$_3$)$_2$), −74.92 (s, $w_{1/2}$ = 62 Hz, 2 H, CH$_2$). IR (Nujol): ν/cm^{-1} 2114 s (N$_3$).

(b) An NMR tube was charged with **7a** (10.7 mg, 13.9 μmol) in pentane (0.5 mL) and 15-crown-5 (2.75 μL, 13.9 μmol) was added, leading to the formation of a yellow orange oil within a few minutes. The mixture was heated for 2 h at 60 °C, and brown crystals of **7b** appeared in the oil.

Synthesis of [NEt$_4$][UN*$_2$(N,C)(CN)] (8a) and Crystals of [Na(15-crown-5)][UN*$_2$(N,C)(CN)] (8b) and [K(18-crown-6)]-[UN*$_2$(N,C)(CN)] (8c). (a) A flask was charged with **1** (105 mg, 146 μmol) and NEt$_4$CN (21.8 mg, 139 μmol), and THF (10 mL) was condensed in. After stirring for 2 d at 20 °C, the brown solution was filtered and evaporated to dryness, leaving a brown oily residue which was washed with a mixture of THF (1 mL) and pentane (10 mL) and then with pentane (10 mL). The greenish-brown powder of **8a** was isolated after drying for 15 h under vacuum. Yield: 105 mg (86%). Anal. calcd for $C_{27}H_{73}N_5Si_6U$: C, 37.09; H, 8.41; N, 8.01. Found: C, 36.76; H, 8.25; N, 7.95. ^{1}H NMR (THF-d_8, 23 °C): δ 31.92 (s, $w_{1/2}$ = 34 Hz, 9 H, SiMe$_3$), 7.64 (s, $w_{1/2}$ = 12 Hz, 6 H, SiMe$_2$), −2.24 (d, 8 H, N(CH$_2$CH$_3$)$_4$), −3.33 (s, 12 H, N(CH$_2$CH$_3$)$_4$), −9.87 (s, $w_{1/2}$ = 18 Hz, 36 H, N(SiMe$_3$)$_2$), −199.21 (s, $w_{1/2}$ = 380 Hz, 2 H, CH$_2$). IR (Nujol): ν/cm^{-1} 2063 m (CN). Crystals of **8a** were formed upon slow diffusion of pentane into a solution of **8a** (10 mg) in THF (0.1 mL).

(b) An NMR tube was charged with **1** (10 mg, 14 μmol) and NaCN (0.7 mg, 14 μmol) in THF (0.5 mL). The solution was stirred for 1 d at 20 °C, and 15-crown-5 (2.75 μL, 13.9 μmol) was added. The volume of the solution was reduced to 0.1 mL, and slow diffusion of pentane into the solution led to the formation, after 5 d, of thin brown crystals of **8b**.

(c) An NMR tube was charged with **1** (10 mg, 14 μmol) and KCN (0.9 mg, 14 μmol) in THF (0.5 mL). The solution was stirred for 1 d at 20 °C, and 18-crown-6 (3.7 mg, 14 μmol) was added. The volume of the solution was reduced to 0.1 mL, and slow diffusion of pentane into the solution led to the formation, after 4 d, of dark brown crystals of **8c**.

Synthesis of Na[UN*(N,N)(N$_3$)$_2$] (9a) and Crystals of [Na-(THF)$_4$][UN*(N,N)(N$_3$)$_2$] (9b). (a) A flask was charged with **4** (100

mg, 118 μmol) and NaN$_3$ (19.3 mg, 296 μmol), and THF (10 mL) was condensed in. After stirring for 4 d at 20 °C, a white precipitate was formed and the reaction mixture was evaporated to dryness. The product was first extracted with THF (10 mL) and, after filtration and evaporation of the solution, with a mixture of THF (1 mL) and Et$_2$O (10 mL). The yellow solution was filtered and evaporated to dryness, leaving the pale brown powder of **9a** which was dried under vacuum for 15 h at 20 °C. Yield: 80 mg (82%). Anal. calcd for $C_{18}H_{52}N_9NaSi_6U$: C, 26.23; H, 6.36; N, 15.29. Found: C, 25.46; H, 5.96; N, 14.81 (these slightly lower values would be due to incomplete combustion of the sample). ^{1}H NMR (THF-d_8, 23 °C): δ 6.12 (s, $w_{1/2}$ = 126 Hz, 6 H, SiMe$_2$), −8.03 (s, $w_{1/2}$ = 13 Hz, 18 H, SiMe$_3$), −9.72 (s, $w_{1/2}$ = 64 Hz, 18 H, SiMe$_3$), −17.80 (s, $w_{1/2}$ = 116 Hz, 6 H, SiMe$_2$), −73.26 (s, $w_{1/2}$ = 23 Hz, 4 H, CH$_2$). IR (Nujol): ν/cm^{-1} 2104 s, br (N$_3$).

(b) A vial was charged with **9a** (5 mg), and THF (2 drops) was added. Slow evaporation of the solution thus obtained afforded pink needles of **9b**.

Synthesis of [NEt$_4$][UN*(N,N)(CN)$_2$] (10). A flask was charged with **4** (100 mg, 118 μmol) and NEt$_4$CN (37.0 mg, 237 μmol), and THF (10 mL) was condensed in. After stirring for 4 d at 20 °C, a white precipitate was formed and the reaction mixture was evaporated to dryness. The product was first extracted with THF (10 mL) and, after filtration and evaporation of the solution, with a mixture of THF (1 mL) and Et$_2$O (10 mL). The yellow solution was filtered and evaporated to dryness, leaving the pale brown powder of **10** which was dried under vacuum for 15 h at 20 °C. Yield: 81 mg (76%). Anal. calcd for $C_{28}H_{72}N_6Si_6U$: C, 37.39; H, 8.07; N, 9.34. Found: C, 36.65; H, 7.79; N, 9.39. ^{1}H NMR (THF-d_8, 23 °C): δ 12.88 (s, $w_{1/2}$ = 32 Hz, 18 H, SiMe$_3$), 3.78 (s, $w_{1/2}$ = 64 Hz, 6 H, SiMe$_2$), 1.73 (s, 8 H, N(CH$_2$CH$_3$)$_4$), −0.05 (s, 12 H, N(CH$_2$CH$_3$)$_4$), −1.54 (s, $w_{1/2}$ = 46 Hz, 6 H, SiMe$_2$), −5.22 (s, $w_{1/2}$ = 96 Hz, 18 H, SiMe$_3$), −61.78 (s, $w_{1/2}$ = 72 Hz, 2 H, CH$_2$), −97.78 (s, $w_{1/2}$ = 104 Hz, 2 H, CH$_2$). IR (Nujol): ν/cm^{-1} 2059 m (CN). An NMR tube charged with **10** (5 mg) in Et$_2$O (1 mL) was heated at 60 °C, and pink needles of **10** were formed after 2 h.

Synthesis of Na[UN*(N,O)$_2$(N$_3$)] (11a) and Crystals of [Na(15-crown-5)][UN*(N,O)$_2$(N$_3$)]·0.5n-Pentane (11b·0.5n-Pentane). (a) A flask was charged with **5** (100 mg, 118 μmol) and NaN$_3$ (10.1 mg, 155 μmol) in THF (10 mL). After 2 d at 20 °C, the solution was filtered and evaporated to dryness, leaving a dark red powder of **11a**. Yield: 97 mg (98%). Anal. calcd for $C_{20}H_{52}N_6NaO_2Si_6U$: C, 28.66; H, 6.25; N, 10.02. Found: C, 28.47; H, 6.25; N, 10.08. ^{1}H NMR (THF-d_8, 23 °C): δ 14.48 (s, $w_{1/2}$ = 100 Hz, 1 H, CH$_2$), 13.39 (s, $w_{1/2}$ = 90 Hz, 1 H, CH$_2$), 11.78 (s, $w_{1/2}$ = 90 Hz, 1 H, CH$_2$), 9.60 (s, $w_{1/2}$ = 70 Hz, 1 H, CH$_2$), 4.27 (s, $w_{1/2}$ = 54 Hz, 6 H, SiMe$_2$), 1.25 (s, $w_{1/2}$ = 55 Hz, 6 H, SiMe$_2$), −1.24 (s, $w_{1/2}$ = 100 Hz, 9 H, SiMe$_3$), −2.94 (s, 9 H, SiMe$_3$), −3.13 (s, 9 H, SiMe$_3$), −3.93 (s, $w_{1/2}$ = 100 Hz, 9 H, SiMe$_3$). IR (Nujol): ν/cm^{-1} 2119 s (N$_3$); 1590 w (C=CH$_2$).

(b) An NMR tube was charged with **11a** (5.4 mg, 6.5 μmol) and 15-crown-5 (1.28 μL, 6.5 μmol) in pentane (0.5 mL). After 12 d at 20 °C, red crystals of **11b** appeared in a red orange oil.

Synthesis of [NEt$_4$][UN*(N,O)$_2$(CN)] (12a) and Crystals of [Na(15-crown-5)][UN*(N,O)$_2$(CN)] (12b) and 12b·0.5n-Pentane. (a) A flask was charged with **5** (105 mg, 136 μmol) and NEt$_4$CN (20.2 mg, 129 μmol), and THF (5 mL) was condensed in. After stirring for 3 d at 20 °C, the solution was filtered and evaporated to dryness, leaving the brown orange powder of **12a** which was washed with pentane (8 mL) and dried under vacuum for 2 h. Yield: 106 mg (88%). Anal. calcd for $C_{29}H_{72}N_5O_2Si_6U$: C, 37.47; H, 7.81; N, 7.53. Found: C, 37.19; H, 7.66; N, 7.65. ^{1}H NMR (THF-d_8, 23 °C): δ 15.93 (s, $w_{1/2}$ = 120 Hz, 1 H, CH$_2$), 14.94 (s, $w_{1/2}$ = 124 Hz, 1 H, CH$_2$), 13.03 (s, $w_{1/2}$ = 120 Hz, 1 H, CH$_2$), 11.02 (s, $w_{1/2}$ = 108 Hz, 1 H, CH$_2$), −1.46 (s, $w_{1/2}$ = 72 Hz, 6 H, SiMe$_2$), −2.21 (s, $w_{1/2}$ = 88 Hz, 6 H, SiMe$_2$), −3.84 (s, $w_{1/2}$ = 64 Hz, 18 H, SiMe$_3$), −4.61 (s, $w_{1/2}$ = 80 Hz, 9 H, SiMe$_3$), −5.20 (s, $w_{1/2}$ = 108 Hz, 9 H, SiMe$_3$). IR (Nujol): ν/cm^{-1} 2059 w, br (CN), 1579 m (C=C).

(b) An NMR tube was charged with **5** (5.0 mg, 6.5 μmol) and NaCN (0.3 mg, 6.5 μmol) in pentane (0.7 mL) and 15-crown-5 (1.28 μL, 6.5 μmol) was added. A dark precipitate was observed after a few

minutes. After 1 d at 60 °C, orange parallelepiped crystals of **12b**·0.5*n*-pentane appeared, and after 8 d at 20 °C, long orange needles of **12b** were formed.

Reaction of 12a with I₂. An NMR tube was charged with **12a** (9.3 mg, 10.0 μmol) and I_2 (1.3 mg, 5.0 μmol) in THF-d_8 (0.7 mL). After 10 min at 20 °C, the ¹H NMR spectrum showed the complete formation of **5**.

Synthesis of [U(N{SiMe₃}SiMe₂C{CHI}O)₂I(THF)] (13). A flask was charged with **11a** (83 mg, 99 μmol) and I_2 (50.3 mg, 198 μmol) in THF (7 mL). After stirring for 15 h at 20 °C, the solvent was evaporated off. The dark red powder was extracted in pentane (5 mL). The solution was cooled at 0 °C, and its volume was slowly reduced to 0.5 mL, leaving dark red crystals of **13** which were washed with pentane (0.5 mL) and dried for 12 h under vacuum. Yield: 28 mg (27%). Anal. calcd for $C_{18}H_{40}I_3N_2O_3Si_4U$: C, 20.33; H, 3.79; N, 2.63. Found: C, 19.95; H, 3.60; N, 2.40. The variable temperature ¹H NMR spectra (from +30 °C to −100 °C) were uninformative due to very large line broadening and overlapping. IR (Nujol): ν/cm^{-1} 1545 w (C=CHI).

Crystallography. The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[11] using graphite-monochromated Mo−Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten 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.[12] Absorption effects were corrected empirically with the program SCALEPACK.[12] The structures were solved by Patterson map interpretation (**8b**, **9b**) or by direct methods (all other compounds) with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[13] The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH_2) or 1.5 (CH_3) times that of the parent atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. In all compounds, restraints on bond lengths, angles, and/or displacement parameters were applied in the disordered parts and/or the badly resolved crown ether moieties and NEt_4 counterions. Special details are as follows:

Compound 7b. The N* and (*C,N*) ligands are heavily disordered: the first (containing N1) displays two positions sharing the nitrogen and one terminal carbon atom (C2), with atom C1A in one of the positions corresponding to a uranium-bound −CH_2 group; the second (containing N2) has one $SiMe_3$ group disordered over two positions, with atom C7A corresponding to a uranium-bound −CH_2 group. Since only one such −CH_2 group must be present for charge equilibrium, these two sets of positions were refined with occupancy parameters constrained to sum to unity (which also accounts for a short H···H contact).

Compound 8a. The N* and (*C,N*) ligands are heavily disordered: the first (containing N1) displays two positions sharing the nitrogen, one silicium, and one terminal carbon atoms, with atom C1A in one of the positions corresponding to a uranium-bound −CH_2 group; the second (containing N2) has one $SiMe_3$ group disordered over two positions, with atom C7A corresponding to a uranium-bound −CH_2 group. As in **7b**, these two sets of positions were refined with occupancy parameters constrained to sum to unity. The third ligand (containing N3) has two positions sharing the nitrogen, one silicium and one terminal carbon atom.

Compound 8c. The crown ether moiety is rotationally disordered over two positions which have been refined with 0.5 occupancy parameters. The two largest residual electron density peaks are located at about 1 Å from the uranium atom; the residual electron density elsewhere is lower than 0.8 e Å⁻³.

Compound 9b. One carbon atom of a THF molecule was found to be disordered over two positions which were refined with occupancy parameters constrained to sum to unity.

Compound 12b·0.5*n*-Pentane. The pentane solvent molecules were given 0.5 occupancy factors in order to retain acceptable displacement parameters.

Crystal data and structure refinement details are given in Table 1. The molecular plots were drawn with ORTEP-3.[14]

■ RESULTS AND DISCUSSION

Oxidation of [UN*₂(*N,C*)] (**1**) and the anionic bismetallacyclic uranium(IV) complexes [NaUN*(*N,C*)₂] (**2**) and [NaUN*-
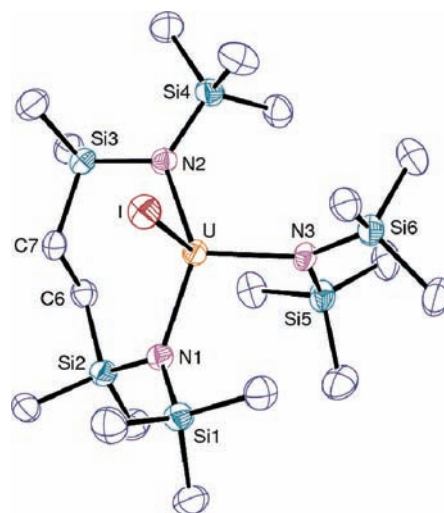

Figure 1. View of **4** with displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms have been omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [UN*(*N,N*)I] (4)

	4
U−N(1)	2.242(2)
U−N(2)	2.235(2)
U−N(3)	2.262(2)
U−I	2.9743(2)
N(1)−U−N(2)	136.05(9)
N(1)−U−N(3)	106.60(8)
N(2)−U−N(3)	107.30(8)
I−U−N(1)	97.92(6)
I−U−N(2)	93.77(6)
I−U−N(3)	113.00(6)

(*N,O*)₂] (**3**) was attempted with various oxidizing agents but only reactions of **2** and **3** with iodine afforded isolable and characterized products. The successful oxidation of electron rich species involving hard oxygen and nitrogen ligands led us to synthesize anionic azide and cyanide U^{IV} and U^V derivatives viewed as potential precursors of new U^V and U^{VI} species with interesting chemical properties. The syntheses are summarized in Scheme 1.

Reactions of the U^{IV} Bismetallacycles [NaUN*(*N,C*)₂] (2) and [NaUN*(*N,O*)₂] (3) with Iodine. *Synthesis of the U^{IV} Enlarged Monometallacycle [UN*(N,N)I] (4) and the U^V Bismetallacycle [Na{UN*(N,O)₂}₂(μ-I)] (5).* No reaction was observed between the neutral monometallacyclic complex [UN*₂(*N,C*)] (**1**) and 1 mol equiv of iodine in benzene at 20 °C, and the slow decomposition of **1** into unidentified products was found to occur in THF. In contrast, the bismetallacycle **2** was readily transformed into the iodo
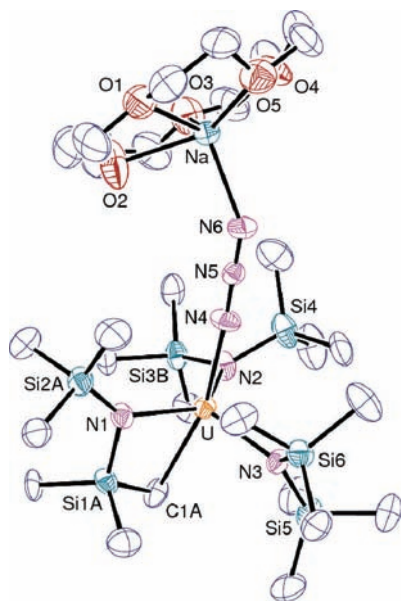
Figure 2. View of **7b** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted. Only one position of the disordered parts is represented.
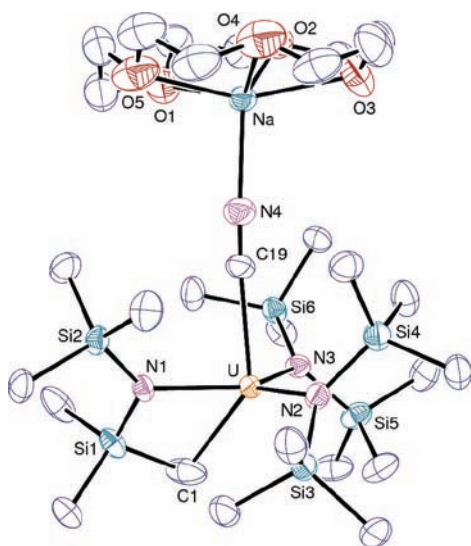

Figure 3. View of **8b** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted.
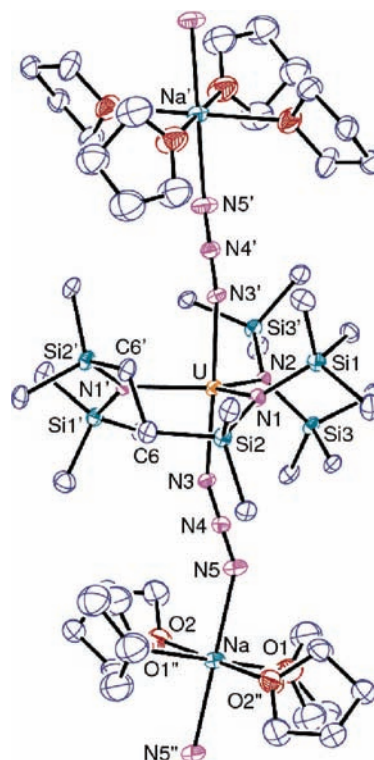

Figure 4. View of **9b** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted. Symmetry codes: ′ = 1 − x, y, $^1/_2$ − z; ″ = $^1/_2$ − x, $^1/_2$ − y, −z.
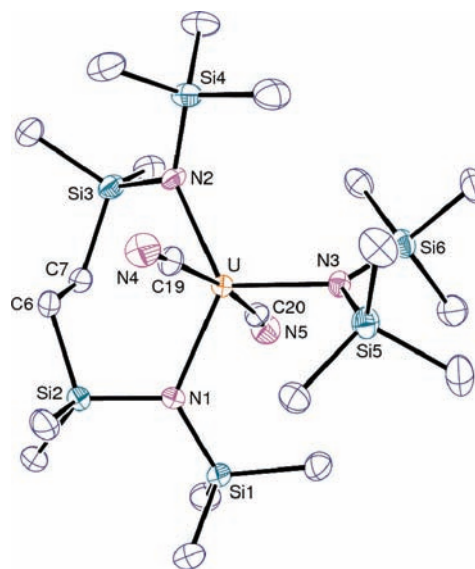

Figure 5. View of the anionic complex in **10** with displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms have been omitted.

derivative **4** in which the (N,N) metallacycle results from C—C coupling of the two CH$_2$ groups. The distinct reactivity of **1** and **2** can be accounted for by the greater nucleophilic character of the U—CH$_2$ bonds in the anionic complex which was previously noted in the CO and CO$_2$ insertion reactions.[6] It seems likely that the first step in the synthesis of **4** is the cleavage of the U—C bond of **2** with iodine, leading to the formation of the intermediate [UN*(N,C)(N{SiMe$_3$}-SiMe$_2$CH$_2$I)],[6] followed by nucleophilic attack of the U—CH$_2$ group onto the activated alkyl iodide CH$_2$I. To the best of our knowledge, such enlargement of metallacycle is unprecedented and a similar (N,N) ligand was encountered only in the zirconium compound [Zr(RNSiMe$_2$CH$_2$CH$_2$SiMe$_2$NR)-(NMe$_2$)$_2$], obtained by reaction of [Zr(NMe$_2$)$_4$] with RNHSiMe$_2$CH$_2$CH$_2$SiMe$_2$NHR (R = 2,6-Me$_2$C$_6$H$_3$).[15] A similar intermolecular C—C coupling was recently reported

with the transformation of the oxo monometallacycle [U^V(═O)N*$_2$(N,C)] into the reduced bimetallic complex [U^{IV}(OSiMe$_3$)(N*)$_2$]$_2$(μ-N{SiMe$_3$}SiMe$_2$CH$_2$CH$_2$SiMe$_2$N-{SiMe$_3$}) in the presence of Me$_3$SiI.[16]

The crystal structure of **4** (Figure 1) has been described in the preliminary communication.[10] The most salient feature is the twist-boat conformation of the seven membered metallacycle with the two carbon atoms in close proximity of the metal center, reflecting the presence of U···H—C γ agostic

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complexes M[UN*$_2$(N,C)X]

X = N$_3$	M = Na*[a] 7b	X = CN	M = NEt$_4$[b] 8a	M = Na* 8b	M = K*[a] 8c
U−C(1A)	2.524(9)	U−C(1)	2.423(7)	2.697(13)	2.516(17)
U−N(1)	2.239(6)	U−N(1)	2.285(3)	2.259(5)	2.258(10)
U−N(2)	2.287(7)	U−N(2)	2.256(3)	2.300(5)	2.293(10)
U−N(3)	2.308(6)	U−N(3)	2.300(4)	2.279(6)	2.280(10)
U−N(4)	2.362(7)	U−C(19)	2.559(4)	2.514(8)	2.457(17)
C(1A)−U−N(1)	72.6(4)	C(1)−U−N(1)	72.9(2)	66.8(3)	69.8(5)
C(1A)−U−N(2)	99.7(4)	C(1)−U−N(2)	96.7(2)	132.6(3)	128.2(5)
C(1A)−U−N(3)	92.0(4)	C(1)−U−N(3)	95.5(2)	84.3(3)	85.9(4)
C(1A)−U−N(4)	163.6(4)	C(1)−U−C(19)	145.7(2)	133.3(4)	130.9(6)
N(2)−U−N(3)	115.7(3)	N(2)−U−N(3)	111.06(16)	116.7(2)	112.5(4)
U−N(4)−N(5)	174.4(7)	U−C(19)−N(4)	172.6(4)	175.1(9)	171.5(16)
N(4)−N(5)	1.164(9)	C(19)−N(4)	1.159(5)	1.150(11)	1.19(2)
N(5)−N(6)	1.156(9)				
N(4)−N(5)−N(6)	178.7(10)				

[a]Na* = Na(15-crown-5); K* = K(18-crown-6). [b]C(1) is labeled C(1A) in **8a** due to disorder within the Me$_3$Si groups.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Na(THF)$_4$][UN*(N,N)(N$_3$)$_2$] (9b) and [NEt$_4$][UN*(N,N)(CN)$_2$] (10)

9b		10	
U−N(1)	2.282(4)	U−N(1)	2.265(5)
U−N(2)	2.257(6)	U−N(2)	2.266(5)
U−N(3)	2.343(4)	U−N(3)	2.267(5)
N(1)−U−N(1')[a]	126.5(2)	U−C(19)	2.485(7)
N(1)−U−N(2)	116.77(10)	U−C(20)	2.519(7)
N(1)−U−N(3)	92.60(16)	N(1)−U−N(2)	130.30(19)
N(2)−U−N(3)	91.83(12)	N(1)−U−N(3)	112.98(19)
N(3)−U−N(3')	176.3(2)	N(2)−U−N(3)	116.48(19)
U−N(3)−N(4)	158.0(4)	N(1)−U−C(19)	90.7(2)
Na−N(5)	2.400(5)	N(1)−U−C(20)	84.5(2)
<Na−O>	2.38(2)	C(19)−U−C(20)	173.5(2)
N(3)−N(4)	1.182(6)	U−C(19)−N(4)	177.7(7)
N(4)−N(5)	1.151(6)	U−C(20)−N(5)	173.8(6)
N(3)−N(4)−N(5)	179.5(7)	C(19)−N(4)	1.136(10)
		C(20)−N(5)	1.159(10)

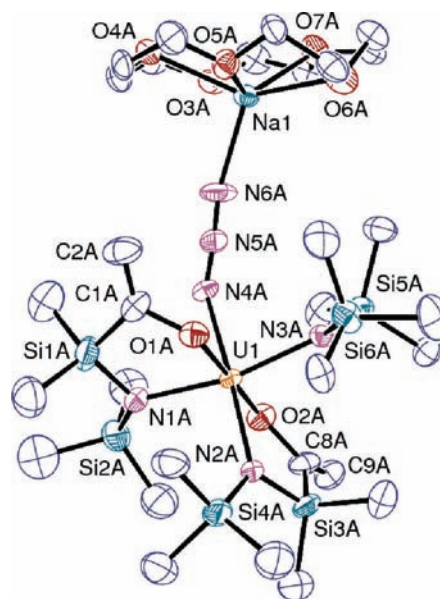[a]Symmetry code: ' = 1 − x, y, $^1/_2$ − z.

Figure 6. View of one of the two independent molecules in **11b** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted.

interactions (Table 2). These interactions are retained in THF solution, as shown by the ^{1}H NMR spectrum in THF-d_8 at −107 °C which exhibits four signals at δ −138.77, −181.48, −373.45, and −493.2, each integrating for 1 H, corresponding to the four distinct hydrogen atoms of the CH$_2$−CH$_2$ fragment. Coalescence of these signals occurs around −70 °C, and two resonances integrating for 2 H are visible at δ −119.57 and −126.10 in the fast limit spectrum at 23 °C, due to the conformational exchange between the two CH$_2$ groups interacting with the U^{IV} ion.

Other attempts at the oxidation of **2** by treatment with various reagents (AgI, TlBPh$_4$, CuCl, C$_5$H$_5$NO, Me$_3$NO) were unsuccessful, leading to intractable products. Only in the case of the reaction with C$_2$Cl$_6$ in THF was obtained a compound which would be the chloro analogue of **4**, in view of the very similar ^{1}H NMR spectra.

Cleavage of the U−C bond in **2** by I$_2$ was clearly an obstacle to the attempted U^{IV} → U^V oxidation and the formation of high valent organometallic species. However, similar reaction of **3** which is devoid of any U−C bond led to the ready formation of [Na{UN*(N,O)$_2$}$_2$(μ-I)] (**5**), isolated as a glassy dark red

material in 81% yield after evaporation of the solution and extraction in pentane. The formulation of **5** as a diuranium(V) "ate" complex was deduced from the ^{1}H NMR spectrum which exhibits broad resonances characteristic of U^V compounds and the elemental analyses which invariably indicate the retention of 0.5 equiv of NaI per uranium for independently prepared samples. The formation of a U^V compound was confirmed by the synthesis and X-ray crystal structure of the cyanide and azide derivatives (vide infra).

The one electron oxidation of **3** into **5** by I$_2$ is similar to that of the anionic U^{IV} alkoxide and chloro-carbene complexes [Li(THF)]$_2$[U(O^{t}Bu)$_6$][7b] and [Li(THF)$_2$][U(C-{Ph$_2$PNSiMe$_3$}$_2$)Cl$_3$][7j] into the corresponding U^V counterparts. Reactions of **3** with other oxidizing reagents such as Me$_3$SiN$_3$, C$_5$H$_5$NO, and NOBF$_4$ were not straightforward and gave unidentified products. Reduction of **5** with sodium amalgam in THF gave back **3** (NMR experiment).
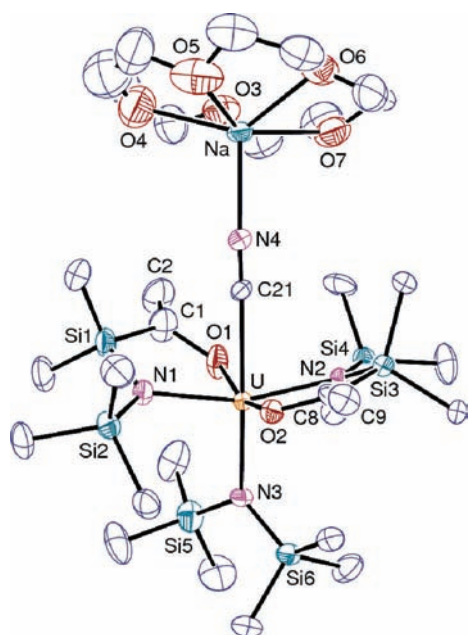
Figure 7. View of **12b** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted.

Reduction of [UN*(N,N)I] (4). *Synthesis of [UN*(N,N)] (6).* Compound **4** was converted into the U^{III} metallacycle **6** upon reduction with 2% Na(Hg) in THF. After stirring for 24 h at 20 °C, the dark purple solution was evaporated to dryness and **6** was extracted in pentane and isolated in almost quantitative yield as a dark purple glassy material. The ^1H
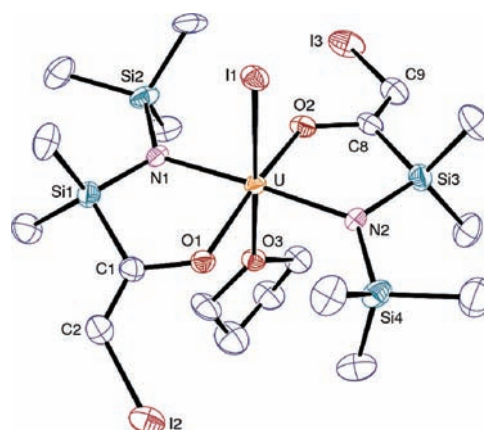

Figure 8. View of **13** with displacement ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted.

NMR spectrum at 23 °C exhibits a broad upfield shifted signal at δ −52.6, integrating for 4 H and corresponding to the CH_2 groups which, as in **4**, are likely involved in U···H−C γ agostic interactions with the paramagnetic metal center. As expected for a U^{III} complex, the NMR resonances of **6** are much broader and less shifted than those of its U^{IV} precursor. In contrast to **4**, the spectrum at −107 °C did not exhibit four signals corresponding to the distinct hydrogen atoms of the CH_2−CH_2 fragment but showed a single broad signal integrating for 4 H at δ −117.8. This difference could reflect the weaker agostic interaction between the γ C−H bond and the more electron rich U^{III} center. Indeed, less shifted signals corresponding to the CH_2−CH_2 fragment are also observed

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Na(15-crown-5)][UN*(N,O)₂(N₃)]·0.5n-pentane (11b·0.5n-pentane), [Na(15-crown-5)][UN*(N,O)₂(CN)] (12b), 12b·0.5n-Pentane, and [U(N{SiMe₃}SiMe₂C{CHI}O)₂I(THF)] (13)

11b·0.5Pentane[a]		12b		12b·0.5Pentane[a]	13	
U−O(1)	2.119(7) [2.102(5)]	U−O(1)	2.060(7)	2.094(6) [2.096(5)]	U−O(1)	2.099(5)
U−O(2)	2.059(6) [2.099(5)]	U−O(2)	2.110(6)	2.062(8) [2.077(6)]	U−O(2)	2.094(6)
U−N(1)	2.250(8) [2.258(6)]	U−N(1)	2.241(6)	2.255(6) [2.236(5)]	U−O(3)	2.405(5)
U−N(2)	2.267(7) [2.301(7)]	U−N(2)	2.235(6)	2.233(6) [2.244(6)]	U−N(1)	2.187(6)
U−N(3)	2.268(7) [2.269(6)]	U−N(3)	2.306(6)	2.294(6) [2.297(5)]	U−N(2)	2.168(6)
U−N(4)	2.369(7) [2.363(8)]	U−C(21)	2.565(7)	2.582(7) [2.572(7)]	U−I(1)	2.9955(6)
N(1)−U−O(1)	84.9(4) [82.7(2)]	N(1)−U−O(1)	82.6(3)	82.7(2) [82.2(2)]	N(1)−U−O(1)	83.4(2)
N(2)−U−O(2)	80.8(3) [81.1(2)]	N(2)−U−O(2)	81.7(2)	83.6(3) [85.4(3)]	N(2)−U−O(2)	84.1(3)
N(1)−U−N(2)	94.9(3) [95.7(3)]	N(1)−U−N(2)	161.5(2)	162.9(2) [162.4(2)]	N(1)−U−N(2)	175.9(2)
N(1)−U−N(3)	167.0(3) [166.5(2)]	N(1)−U−N(3)	98.1(2)	98.1(2) [97.4(2)]	N(1)−U−O(3)	87.4(2)
N(2)−U−N(4)	173.7(4) [171.7(3)]	N(2)−U−C(21)	80.7(2)	81.1(2) [81.8(2)]	N(2)−U−I(1)	92.50(18)
N(3)−U−N(4)	85.6(3) [85.6(2)]	N(3)−U−C(21)	178.1(2)	179.3(3) [177.4(2)]	O(3)−U−I(1)	178.98(14)
O(1)−U−O(2)	177.4(3) [176.1(2)]	O(1)−U−O(2)	160.4(3)	159.9(4) [164.8(3)]	O(1)−U−O(2)	168.0(2)
U−N(4)−N(5)	126.4(7) [140.2(6)]	U−C(21)−N(4)	178.5(6)	177.9(6) [179.5(7)]	C(2)−I(2)	2.035(12)
N(4)−N(5)	1.204(12) [1.174(10)]	C(21)−N(4)	1.142(9)	1.146(8) [1.153(8)]	C(9)−I(3)	2.038(12)
N(5)−N(6)	1.167(13) [1.155(11)]	Na−N(4)	2.350(7)	2.348(7) [2.344(6)]		

[a] Values for the two independent molecules.

in the NMR spectra of the anionic azide and cyanide U^{IV} derivatives of **4** (vide infra). Although **6** did not crystallize, its treatment with NaCN in THF, followed by addition of 15-crown-5 in pentane, afforded dark purple crystals of the U^{III} bimetallic complex $[Na(15\text{-crown-}5)][\{U(N,N)N^*\}_2(\mu\text{-CN})]$ together with other unidentified products. The crystal structure of this later will be detailed in a forthcoming paper.

Synthesis and Crystal Structure of the Azide and Cyanide Compounds $[UN^*_2(N,C)X]^-$, $[UN^*(N,N)X_2]^-$, and $[UN^*(N,O)_2X]^-$ (X = N$_3$, CN). The anionic azide and cyanide compounds were synthesized in view of their further oxidation into U^V and U^{VI} derivatives, and also for their potential as precursors of polymetallic species. Treatment of **1** with 1 mol equiv of NaN$_3$ in THF gave, after filtration and evaporation of the reaction mixture, a brown powder of $Na[UN^*_2(N,C)(N_3)]$ (**7a**) in almost quantitative yield (Scheme 1). Heating a solution of **7a** and 15-crown-5 in pentane led to the formation of brown crystals of $[Na(15\text{-crown-}5)][UN^*_2(N,C)(N_3)]$ (**7b**). Similar reaction of **1** with NEt$_4$CN in THF afforded a greenish-brown powder of $[NEt_4][UN^*_2(N,C)(CN)]$ (**8a**) in 86% yield, and crystals of **8a** were obtained upon slow diffusion of pentane into a THF solution. Brown crystals of $[Na(15\text{-crown-}5)][UN^*_2(N,C)(CN)]$ (**8b**) and $[K(18\text{-crown-}6)][UN^*_2(N,C)(CN)]$ (**8c**) were formed when pentane was diffused into a THF solution of a 1:1:1 mixture of **1**, NaCN, and 15-crown-5, or **1**, KCN, and 18-crown-6, respectively.

Treatment of the (N,N) metallacycle **4** with NaN$_3$ or NEt$_4$CN in THF led to the substitution of the iodide group of **4** together with addition of a second N$_3^-$ or CN$^-$ ligand, so that 2 mol equiv of the azide or cyanide salt were necessary for the complete formation of $Na[UN^*(N,N)(N_3)_2]$ (**9a**) or $[NEt_4]$-$[UN^*(N,N)(CN)_2]$ (**10**). After filtration and evaporation of the reaction mixture, **9a** and **10** were extracted in THF−Et$_2$O and isolated as pale brown powders in 82 and 76% yields, respectively. Slow evaporation of a THF solution of **9a** gave pink needles of $[Na(THF)_4][UN^*(N,N)(N_3)_2]$ (**9b**) while pink needles of **10** were formed by heating a suspension of the compound in diethyl ether.

Views of the (N,C) metallacycles **7b**, **8b**, and the (N,N) metallacycles **9b** and **10** are presented in Figures 2−5, and selected bond lengths and angles of these complexes and **8a** and **8c** are listed in Tables 3 and 4, respectively. Some N* and (C,N) ligands are strongly disordered in **7b** and **8a**, with the coordinated −CH$_2$ group being distributed over two different ligands (see details in the Experimental Section). The uranium atom is five-coordinate in all complexes, but while its environment in **7** and **8** is intermediate between a trigonal bipyramid (with N(1), N(2), and N(3) defining the basis) and a square pyramid (with N(1), N(2), N(3), and C(1) defining the basis), complexes **9b** and **10** adopt a quite perfect trigonal bipyramidal configuration, with the nitrogen atoms of the (N,N) and N* ligands forming the basis. This difference can be explained by the very distinct bite angles of the (N,C) and (N,N) chelates, ca. 70° and 130°, respectively, and is in line with the expected theoretical stereochemistry for complexes of the type $[M(\text{bidentate})(\text{unidentate})_3]$.[17] The (N,C) ligands are planar while the (N,N) cycles adopt a twist boat conformation in which the C_2 axis passes through the U atom and the middle of the CH$_2$−CH$_2$ fragment. In the case of **9b**, this axis is a crystallographically imposed 2-fold axis of symmetry and the 1D polymeric structure resembles that of $[Na(THF)_4]$-$[UN^*_3(N_3)_2]$.[8n] The U−C(1) distances in **7b**, **8a**, and **8c**, with an average value of 2.50(5) Å, are quite identical to those

found in the series of the anionic bismetallacycles $[ML_xUN^*(N,C)_2]$ (M = Li, Na, or K and L = THF or crown ether),[6] which vary from 2.436(6) to 2.545(6) Å and to that of 2.52(2) Å in $[U(N,C)(C_5Me_5)_2]$,[18] but the U−C(1) distance of 2.697(13) Å in **8b** is abnormally long. The U−N(N,C) distances average 2.28(2) Å in complexes **7b** and **8a−c** and are in the range of those measured in the aforementioned (N,C) metallacycles which are comprised between 2.230(5) and 2.343(5) Å. The average U−N(N,N) distance of 2.273(8) Å in **9b** and **10** is slightly larger than that of 2.238(5) Å in the tetra-coordinate compound **4**. The U−N(N*) bond lengths, with a mean value of 2.28(2) Å for all complexes, is typical of terminally coordinated amide ligands.[19] The N$_3$ ligands in **7b** and **9b** are in bridging positions between the U and Na atoms, with U−N(N$_3$) distances of 2.362(7) and 2.343(4) Å and U−N$_\alpha$−N$_\beta$ angles of 174.4(7) and 158.0(4)° which can be compared with those of 2.337(6) Å and 163.9(5)° in $[Na(THF)_4][UN^*_3(N_3)_2]$.[8n] These values are in the range of U−N distances (2.22−2.56 Å) and U−N$_\alpha$−N$_\beta$ angles (121−179°) found in other structurally characterized uranium(IV) azides.[8] The azide moieties are linear with quite equivalent N−N distances [average 1.163(12) Å], likely reflecting the ionic character of the U−N(N$_3$) interaction. The U−C(CN) distances in **8a−c** and **10** which are ranging between 2.457(17) and 2.559(4) Å with an average value of 2.50(4) Å can be compared with those measured in the other anionic U^{IV} cyanide compounds, 2.591(11) Å in $[Mg(THF)_4][U$-$(C_5Me_5)_2Cl_2(\mu\text{-CN})]_2$,[9f] 2.52(1) Å in $[N^nBu_4][U$-$(C_5Me_5)_2(CN)_3]$,[9f] 2.62(2) Å in $[NEt_4]_3[U(C_5Me_5)_2(CN)_5]$,[9f] and 2.626(4) Å in $[NEt_4][(C_8H_8)_2U(CN)]$.[9g] The mean C−N bond length of 1.16(2) Å is identical with that measured in the free cyanide anion.[20]

The azide compound $Na[UN^*(N,O)_2(N_3)]$ (**11**) was isolated in almost quantitative yield as a dark red powder by reaction of **5** with a slight excess of NaN$_3$ in THF, and red crystals of $[Na(15\text{-crown-}5)][UN^*(N,O)_2(N_3)] \cdot 0.5n\text{-pentane}$ (**11b·0.5n-pentane**) were formed upon addition of the crown ether into a pentane solution. After $[Li(THF)_3][U$-$(OAr)_5(N_3)]$ (Ar = 2,6-Me$_2$C$_6$H$_3$) and $[UN^*_3(N_3)_2]$[8n] which have been recently obtained by oxidation of the corresponding di- and monoanionic precursors by silver salts, **11** is a novel example of a U^V azide. Similar treatment of **5** with NEt$_4$CN afforded an orange powder of $[NEt_4][UN^*(N,O)_2(CN)]$ (**12a**) in 88% yield. Orange parallelepiped crystals of $[Na(15\text{-crown-}5)][UN^*(N,O)_2(CN)] \cdot 0.5n\text{-pentane}$ (**12b·0.5n-pentane**) were formed upon heating for 24 h at 60 °C a 1:1:1 mixture of **5**, NaCN and 15-crown-5 in pentane, and orange long needles of **12b** were deposited when the solution was left at 20 °C for 8 days. Complex **12** is the second cyanide compound of uranium(V), after the metallocene $[NBu_4]_2[U$-$(C_5Me_5)_2(CN)_5]$[9c,f] which was characterized only by its crystal structure.

Views of one of the two independent and very similar molecules of the azide **11b**, already presented in the preliminary communication, and of the cyanide **12b** are shown in Figures 6 and 7, respectively, and selected bond lengths and angles are listed in Table 5. These six-coordinate compounds of the type $[M(\text{bidentate})_2(\text{unidentate})_2]$ adopt distinct stereochemistries, ca. *cis*-octahedral for **11b** and *trans*-octahedral for **12b**. The distances between the metal and the nitrogen atoms of the (N,O) and N* ligands, which average 2.26(2) Å for all molecules, and the average U−O distance of 2.09(2) Å are 0.05 Å smaller than those measured in $[Na(15\text{-crown-}5)]$-

$[UN^*(N,O)_2]$,[6] reflecting the variations in the radii of the U^{IV} and U^V ions and the coordination numbers.[21] The average U—$N(N_3)$ bond length of 2.366(3) Å in **11b** is slightly larger than those of 2.318(8) and 2.226(3) Å in the U^V azides $[Li(THF)_3][U(OAr)_5(N_3)]$ and $[UN^*_3(N_3)_2]$.[8n] The average U—C(21) distance of 2.573(7) Å in **12b** and its solvate can be compared with the mean U—C(CN) distance of 2.548(7) Å in $[NBu_4]_2[U(C_5Me_5)_2(CN)_5]$[9c] and is slightly larger than that of 2.514(8) in **8b**, in line with the variation in the oxidation states and coordination numbers. The structural parameters of the N_3 and CN ligands are identical to those in complexes **7**−**10**.

Reactions of $[UN^*(N,O)_2X]^-$ (X = N_3, CN) with I_2. *Synthesis and Crystal Structure of $[U(N\{SiMe_3\}SiMe_2C-\{CHI\}O)_2I(THF)]$ (13).* First attempts at the oxidation of the anionic azide and cyanide complexes **7**−**12** were focused on **11** and **12** in view to reach the +6 oxidation state of uranium. In the presence of 0.5 equiv of iodine in THF, the cyanide **12a** was converted back into the iodide **5**. In contrast, the azide **11a** was transformed under similar conditions into the neutral U^V complex $[U(N\{SiMe_3\}SiMe_2C\{CHI\}O)_2I(THF)]$ (**13**) which was isolated in 27% yield as dark red crystals after evaporation of the solution, extraction in pentane, and crystallization from this solvent. Direct addition of I_2 to the C=C bond of **11a** is not likely since it was not observed with **5** and **12a** and because such halogen addition to alkenes is facile only with Cl_2 or Br_2. The synthesis of **13** can be explained by the initial formation of IN_3, which is known to add efficiently to alkenes under mild conditions.[22] Subsequent elimination of HN_3 would induce protonolysis of the U—N(N*) bond to give the intermediate $Na[U(O,N)(N\{SiMe_3\}SiMe_2C\{CHI\}O)(N_3)I]$; this latter would be transformed into **13** by following the same series of reactions and elimination of NaI.

The crystal structure of **13** was described in the preliminary communication.[10] The complex adopts a *trans*-octahedral configuration (Figure 8). The most salient feature (Table 5) is the U—I(1) distance of 2.9955(6) Å which can be compared with those of 3.1385(6) Å in $[U(N^tBu)_2I(^tBu_2bpy)]$ ($^tBu_2bpy$ =4,4′-di-^{t}Bu-2,2′-bipyridyl)[23] and 3.085(7) and 3.0116(6) Å in $[U(C_5Me_5)_2(NAr)I]$ (Ar = 2,6-$^iPr_2$—C_6H_3 or 2,4,6-$^tBu_3$—C_6H_2),[24] the other uranium(V) iodides to have been crystallographically characterized. The average U—O(N,O) distance of 2.097(3) Å is similar to those measured in **11b** and **12b** while the U—N bonds are shorter, by ca. 0.1 Å, suggesting that the U—N bond is more influenced by the electronic richness of the compound than the U—O bond.

CONCLUSION

Reactions of the metallacycles **1**, **2**, and **3** with iodine were found to follow distinct courses and afforded unexpected products, revealing the rich potential reactivity of the anionic bis metallacyclic uranium compounds. While the neutral (N,C) precursor **1** gave intractable products, **2** afforded the larger U^{IV} (N,N) metallacycle **4** through C−C coupling of its two CH_2 groups. Thus, oxidation of alkyl metallacycle complexes with I_2 is disfavored over metal−carbon cleavage. In contrast, compound **3** which contains only strong U−O and U−N bonds favorable to the stabilization of high-valent species was rapidly oxidized into the stable diuranium(V) compound **5**. Addition of azide and cyanide anions to the sterically unsaturated (N,C) and (N,N) U^{IV} metallacycles **1** and **4** and on the pentavalent bimetallic (N,O) metallacycle **5** afforded anionic derivatives of relevance for new insights into high-valent uranium chemistry. Initial attempt at $U^V \rightarrow U^{VI}$

oxidation of the anionic azide complex **11** with iodine afforded the unexpected neutral uranium(V) iodide complex **13** in which the iodide ligand and the exocyclic C=CHI unit likely result from initial formation of IN_3. Compounds **7**−**12** are promising precursors of U^V and U^{VI} derivatives, since the N_3^- and CN^- ligands are known to stabilize high-valent metal species and because of the capacity of some photochemically activated azido complexes to lose nitrogen toward the formation of nitride derivatives.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Crystallographic data in CIF format and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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