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Preparation and Crystal Structure of the 1,2-Dimethoxyethane Complex of Bis[bis(trimethylsilyl)amido]dichlorouranium(IV)

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The complex $[(Me_3Si)_2N]_2UCl_2$(1,2-dimethoxyethane) has been prepared from uranium tetrachloride and 2 mol equiv of sodium bis(trimethylsilyl)amide in 1,2-dimethoxyethane. It may also be prepared from uranium tetrachloride and 2 mol equiv of sodium bis(trimethylsilyl)amide in tetrahydrofuran followed by addition of 1,2-dimethyoxyethane. The green pentane-soluble complex crystallizes in space group *Pbca* with cell dimensions $a = 15.207$ (4) Å, $b = 12.021$ (3) Å, and $c = 33.427$ (9) Å, with $Z = 8$ and $d_x = 1.57$ g cm^{-3}. The uranium atom, with approximate C_2 local symmetry, is coordinated to two nitrogen atoms from the amide groups, two oxygen atoms from the dimethoxyethane group, and two chlorine atoms. The average U-N, U-O, and U-Cl distances are 2.23, and 2.59, and 2.64 Å, respectively.

Introduction

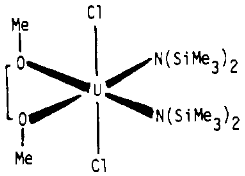
The tris[bis(trimethylsilyl)amido] derivatives of the actinide metals of the type $[(Me_3Si)_2N]_3MCl$, where M is thorium or uranium,[1] have given rise to a series of alkyl and hydride[2] derivatives that have a rich reaction chemistry.[3] The analogous group 4B metal alkyl derivatives $[(Me_3Si)_2N]_3MMe$, where M is zirconium or hafnium, have also been described.[4] The bis(silylamido) derivatives of the group 4B metal alkyls of the type $[(Me_3Si)_2N]_2MR_2$, where M is zirconium or hafnium, also have an extensive reaction chemistry.[5,6] As part of a study of the comparative chemistry of the organometallic compounds of the transition-metal group 4B series relative to those of the actinide series, we have prepared bis[bis(trimethylsilyl)amido]dichlorouranium(IV) and describe the crystal structure of its 1,2-dimethoxyethane complex.

Results and Discussion

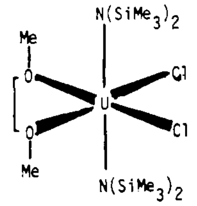
Addition of 2 mol equiv of sodium bis(trimethylsilyl)amide to a tetrahydrofuran solution of uranium tetrachloride followed by crystallization from pentane yields microcrystals of $[(Me_3Si)_2N]_2UCl_2$. Addition of 1,2-dimethoxyethane to the dichloro species yields $[(Me_3Si)_2N]_2UCl_2{\cdot}DME$ (dimethoxyethane = DME) as green prisms from pentane. The 1,2-dimethoxyethane complex may be prepared directly from 2 mol equiv of sodium bis(trimethylsilyl)amide and uranium tetrachloride in 1,2-dimethoxyethane. It is noteworthy that reaction of 2 mol equiv of lithium bis(trimethylsilyl)amide and uranium tetrachloride in tetrahydrofuran affords the tris derivative $[(Me_3Si)_2N]_3UCl$.[1] The bis thorium analogue $[(Me_3Si)_2N]_2ThCl_2$ could not be prepared; all attempted preparations yielded the trisderivative $[(Me_3Si)_2N]_3ThCl$.[1] The latter result is doubtless related to the insolubility of $ThCl_4$ in tetrahydrofuran.

The structure of the (1,2-dimethoxyethane)uranium species is of considerable interest. Three geometrical isomers based upon a cis octahedron are possible (I, II, or III).

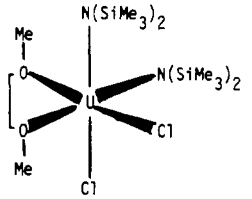
Infrared spectroscopy cannot distinguish between I or II though it is capable of distinguishing among I or II and III, in theory. In practice, the low symmetry of the possible isomers and the difficulty associated with making accurate assignments of metal-nitrogen, metal-oxygen, and metal-chloride stretching frequencies makes this technique unreliable. Fortunately the complex yields crystals suitable for an X-ray examination. This technique shows I to be the correct isomer.



I



II



III

The complex has approximate C_2 symmetry (see Figure 1). The uranium atom has six neighbors: two oxygen atoms of the dimethoxyethane ligand, two nitrogen atoms of the amide ligands, and two chloride ions. The oxygen and nitrogen atoms are approximately coplanar[7] with the uranium atom while the chloride ions are above and below this plane and bent toward the DME ligand.

The DME ligand exhibits considerable thermal motion, and the bond angles and distances reported for this ligand in Tables II and III represent the geometry of the average positions rather than realistic molecular dimensions. In our study of $[(Me_3Si)_2N]_2Eu(DME)_2$,[8] we observed a similar problem with the DME ligand, and in that structure the DME ligand had to be described as a disordered group. The U-O distances of 2.585 and 2.603 Å are unusually large and perhaps reflect the steric effects caused by the crowding of the large (trimethylsilyl)amide ligands on the chloride ions which in turn push on the DME ligand.

Each Si_2NU group is planar, and the average U-N bond distance, 2.235 Å, is consistent with other terminally bonded amide U-N distances such as 2.24 Å in $HU[N(SiMe_3)_2]_3$,[9] 2.21 Å in $U_3(CH_3NCH_2CH_2NCH_3)_6$,[10] 2.27 Å in U[N(C$_6$-

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[1] Turner, H. W.; Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1979** *18*, 1221.

[2] Turner, H. W.; Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1979** *101*, 2782.

[3] Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979** *101*, 7728.

[4] Andersen, R. A. *Inorg. Chem.* **1979** *18*, 1724.

[5] Andersen, R. A. *Inorg. Chem.* **1979** *18*, 2928.

[6] Andersen, R. A. *J. Organomet. Chem.* **1980**, *192*, 189.

[7] The deviations of some of the atoms from the least-squares plane defined by O(1), O(2), N(1), and N(2) are as follows: O(1), 0.18 Å; O(2), -0.20 Å; N(1), 0.14 Å; N(2), -0.13 Å; U, 0.03 Å; Cl(1), 2.61 Å; Cl(2), -2.53 Å.

[8] Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551.

[9] Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 622.

[10] Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 599.

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Table I. Positional Parameters[a]

	x	*y*	*z*
U	0.02718 (2)	0.19019 (3)	0.10858 (1)
Cl(1)	0.1790 (2)	0.2939 (3)	0.0997 (1)
Cl(2)	−0.0998 (2)	0.0519 (2)	0.0891 (1)
Si(1)	0.1459 (2)	0.1119 (3)	0.1966 (1)
Si(2)	−0.0504 (2)	0.1209 (3)	0.2002 (1)
Si(3)	−0.0302 (2)	0.4601 (2)	0.1198 (1)
Si(4)	−0.1417 (2)	0.3459 (3)	0.0591 (1)
O(1)	0.0737 (5)	0.1595 (7)	0.0345 (2)
O(2)	0.1037 (5)	0.0032 (7)	0.0928 (3)
N(1)	0.0455 (4)	0.1339 (6)	0.1716 (2)
N(2)	−0.0531 (4)	0.3397 (6)	0.0924 (2)
C(1)	0.2382 (8)	0.074 (1)	0.1625 (4)
C(2)	0.1828 (8)	0.238 (1)	0.2257 (5)
C(3)	0.142 (1)	−0.006 (1)	0.2315 (6)
C(4)	−0.1427 (7)	0.203 (1)	0.1773 (4)
C(5)	−0.0387 (8)	0.175 (1)	0.2519 (4)
C(6)	−0.089 (1)	−0.027 (1)	0.2036 (5)
C(7)	0.0324 (8)	0.425 (1)	0.1658 (4)
C(8)	0.038 (1)	0.561 (1)	0.0904 (5)
C(9)	−0.132 (1)	0.532 (1)	0.1397 (4)
C(10)	−0.2472 (7)	0.312 (1)	0.0847 (4)
C(11)	−0.1319 (8)	0.247 (1)	0.0152 (4)
C(12)	−0.151 (1)	0.487 (1)	0.0345 (4)
C(13)	0.0950 (9)	0.257 (1)	0.0090 (4)
C(14)	0.0802 (9)	−0.099 (1)	0.1132 (5)
C(15)	0.134 (1)	0.065 (2)	0.0288 (6)
C(16)	0.119 (1)	−0.021 (2)	0.0514 (5)
H(1)	0.256 (8)	0.125 (7)	0.143 (3)
H(2)	0.221 (8)	0.006 (6)	0.150 (3)
H(3)	0.282 (6)	0.064 (8)	0.182 (2)
H(4)	0.133 (5)	0.25 (1)	0.242 (3)
H(5)	0.187 (7)	0.27 (1)	0.203 (2)
H(6)	0.232 (4)	0.22 (1)	0.240 (3)
H(7)	0.130 (6)	−0.073 (7)	0.219 (3)
H(8)	0.100 (5)	0.009 (9)	0.253 (3)
H(9)	0.198 (4)	−0.015 (9)	0.246 (3)
H(10)	−0.164 (7)	0.183 (9)	0.151 (2)
H(11)	−0.146 (7)	0.284 (4)	0.178 (3)
H(12)	−0.192 (6)	0.180 (8)	0.194 (3)
H(13)	−0.024 (6)	0.251 (5)	0.249 (4)
H(14)	0.009 (5)	0.138 (8)	0.267 (3)
H(15)	−0.089 (4)	0.162 (8)	0.268 (3)
H(16)	−0.057 (6)	−0.091 (7)	0.214 (3)
H(17)	−0.096 (7)	−0.05 (1)	0.176 (1)
H(18)	−0.149 (4)	−0.035 (9)	0.214 (3)
H(19)	0.082 (5)	0.383 (7)	0.159 (3)
H(20)	−0.005 (6)	0.378 (7)	0.182 (3)
H(21)	0.047 (7)	0.487 (6)	0.182 (3)
H(22)	0.005 (6)	0.609 (8)	0.074 (3)
H(23)	0.085 (5)	0.531 (9)	0.075 (3)
H(24)	0.059 (7)	0.599 (9)	0.113 (2)
H(25)	−0.163 (7)	0.476 (7)	0.156 (3)
H(26)	−0.173 (6)	0.553 (8)	0.120 (2)
H(27)	−0.116 (7)	0.590 (6)	0.156 (3)
H(28)	−0.247 (7)	0.362 (7)	0.107 (2)
H(29)	−0.250 (7)	0.238 (5)	0.097 (3)
H(30)	−0.302 (5)	0.321 (8)	0.071 (3)
H(31)	−0.103 (6)	0.176 (5)	0.017 (3)
H(32)	−0.091 (5)	0.289 (8)	−0.003 (3)
H(33)	−0.180 (5)	0.238 (9)	−0.004 (3)
H(34)	−0.097 (4)	0.50 (1)	0.021 (3)
H(35)	−0.166 (6)	0.544 (8)	0.053 (3)
H(36)	−0.193 (5)	0.48 (1)	0.014 (2)

[a] Estimated standard deviations of the least significant digits are given in parentheses in this and in the following table.

$H_5)_2]_4$[11] and 2.22 Å in $U[N(C_2H_5)_2]_4$.[12]

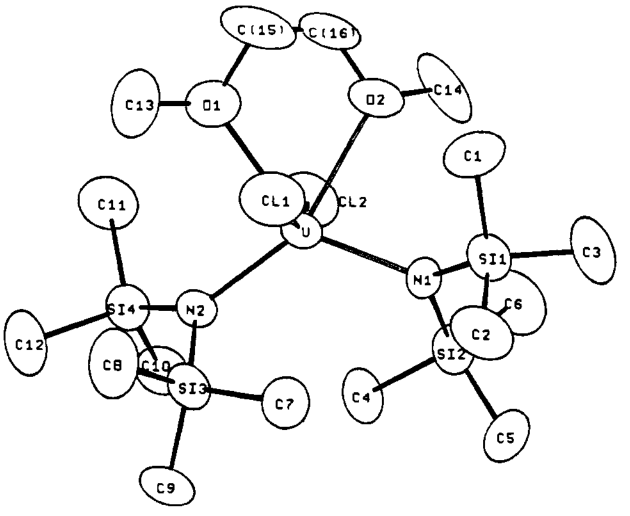

Figure 1. ORTEP view of the structure.

Table II. Interatomic Distances (Å)

U-N(1)	2.231 (8)	Si(2)-C(4)	1.88 (1)
U-N(2)	2.238 (7)	Si(2)-C(5)	1.86 (2)
U-O(1)	2.603 (8)	Si(2)-C(6)	1.88 (2)
U-O(2)	2.585 (8)	Si(3)-C(7)	1.86 (2)
U-Cl(1)	2.640 (3)	Si(3)-C(8)	1.87 (2)
U-Cl(2)	2.630 (3)	Si(3)-C(9)	1.89 (2)
N(1)-Si(1)	1.759 (8)	Si(4)-C(10)	1.86 (1)
N(1)-Si(2)	1.749 (8)	Si(4)-C(11)	1.89 (1)
N(2)-Si(3)	1.749 (8)	Si(4)-C(12)	1.90 (1)
N(2)-Si(4)	1.751 (8)	O(1)-C(13)	1.48 (2)
Si(1)-C(1)	1.86 (2)	O(1)-C(15)	1.46 (2)
Si(1)-C(2)	1.89 (2)	O(2)-C(14)	1.45 (2)
Si(1)-C(3)	1.84 (2)	O(2)-C(16)	1.44 (2)
		C(15)-C(16)	1.30 (2)

Table III. Selected Angles (Deg)

Cl(1)-U-Cl(2)	155.9 (1)	O(1)-U-O(2)	63.9 (3)
Cl(1)-U-O(1)	73.9 (2)	U-N(1)-Si(1)	126.9 (4)
Cl(1)-U-O(2)	89.7 (2)	U-N(1)-Si(2)	116.0 (4)
Cl(2)-U-O(1)	82.8 (2)	Si(1)-N(1)-Si(2)	116.8 (5)
Cl(2)-U-O(2)	74.4 (2)	U-N(2)-Si(3)	115.4 (4)
Cl(1)-U-N(1)	98.1 (2)	U-N(2)-Si(4)	127.5 (4)
Cl(1)-U-N(2)	94.1 (2)	Si(3)-N(2)-Si(4)	116.8 (4)
Cl(2)-U-N(1)	97.7 (2)	U-O(1)-C(13)	119.6 (7)
Cl(2)-U-N(2)	92.7 (2)	U-O(1)-C(15)	113.7 (9)
N(1)-U-N(2)	122.7 (3)	C(13)-O(1)-C(15)	113.5 (11)
N(1)-U-O(1)	145.3 (3)	U-O(2)-C(14)	122.1 (8)
N(1)-U-O(2)	82.7 (3)	U-O(2)-C(16)	116.6 (9)
N(2)-U-O(1)	91.8 (3)	C(14)-O(2)-C(16)	108.7 (12)
N(2)-U-O(2)	153.4 (3)		

The geometry of the complex was initially surprising since our intuition suggested that the two sterically large $(Me_3Si)_2N$ groups would occupy trans positions (II) rather than cis ones (I) in a cis octahedral arrangement. The observed geometry can be rationalized by reference to Kepert's point-on-a-sphere model.[13] In a molecule of the type $M(bidentate)A_2B_2$ (IV),

IV

C = oxygen atoms of 1,2-dimethoxyethane
A = Cl
B = $N(SiMe_3)_2$
M = uranium

the location of the A atoms relative to the B atoms is dictated

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(11) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090.

(12) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498.

(13) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.

by the M–A and M–B bond distances. Monodentate ligands that have the shortest metal–ligand bond lengths will occupy the less sterically crowded B sites in complexes where the normalized bite of the chelating ligand is small. The average uranium–nitrogen bond length in $[(Me_3Si)_2N]_2UCl_2\cdot(1,2\text{-DME})$ (2.34 Å) is shorter than the uranium–chloride bond length (2.63 Å) and the normalized bite (the distance between donor atoms in the chelate group divided by the metal–donor atom distance) of 1,2-dimethoxyethane is 1.06. Thus, the observed geometry is in accord with the Kepert's model.

Experimental Section

Analyses were by the microanalytical laboratory of this department. The ^1H nuclear magnetic resonance spectra were recorded on a JEOL FX-90 machine operating at 90 MHz and are reported in δ values (Me_4Si, δ 0). All operations were performed under nitrogen.

Bis[bis(trimethylsilyl)amido]dichlorouranium(IV). Sodium bis(trimethylsilyl)amide (3.5 g, 0.019 mol) in tetrahydrofuran (20 mL) was added to a solution of uranium tetrachloride (3.6 g, 0.0095 mol) in tetrahydrofuran (25 mL). The suspension was stirred at room temperature for 12 h. The tetrahydrofuran was removed in vacuum, and the gummy solid was exposed to vacuum for 24 h. The residue was extracted with pentane (80 mL), filtered, concentrated in vacuum to ca. 25 mL, and cooled (−70 °C). The pink needles were isolated and dried in vacuum whereupon they turned to microcrystals; mp 77–79 °C. yield was 4.8 g (80%). Anal. Calcd for $C_{12}H_{36}Cl_2N_2Si_4U$: C, 22.9; H, 5.72; Cl, 11.3; N, 4.45. Found: C, 23.7; H, 5.56; Cl, 8.22; N, 4.54. The infrared spectrum in the 500–200 cm^{-1}-region (Nujol mull) consisted of medium-intensity absorptions at 380, 280, and 260 cm^{-1}. The ^1H NMR spectrum (PhH, 30 °C) was a singlet at δ −1.23.

Bis[bis(trimethylsilyl)amido]dichlorouranium(IV)-1,2-Dimethoxyethane. Sodium bis(trimethylsilyl)amide (4.8 g, 0.026 mol) in 1,2-dimethoxyethane (75 mL) was added to a suspension of uranium tetrachloride (4.9 g, 0.013 mol) in 1,2-dimethoxyethane (200 mL). The mixture was stirred at room temperature for 24 h. The 1,2-dimethoxyethane was removed in vacuum, and the residue was extracted with pentane (2 × 100 mL). The combined extracts were filtered, concentrated to ca. 150 mL, and cooled (−10 °C). The green prisms were collected and dried in vacuum; yield was 4.6 g (48%), mp 137–138 °C dec. Anal. Calc for $C_{16}H_{46}Cl_2N_2O_2Si_4U$: C, 26.7; H, 6.44; Cl, 9.85; N, 3.89. Found: C, 27.1; H, 6.55; Cl, 9.84; N, 3.91. The infrared spectrum (Nujol mull) consisted of absorptions at 388 s, 310 w, 290 w, and 255 m cm^{-1}. The ^1H NMR($PhMe\text{-}d_8$) was temperature dependent. At 30 °C a broad resonance centered at δ 0.75, $\nu_{1/2}$ = 160 Hz, was observed, though sharp singlets were observed at 90 and -62 °C.

resonance (90 °C)	assignt	resonance (−62 °C)
−0.84	$(Me_3Si)_2N$	0.31
13.6	MeO	1.11
−13.3	CH_2O	1.37

The 1,2-dimethoxyethane complex can also be prepared by stirring $[(Me_3Si)_2N]_2UCl_2$ in 1,2-dimethoxyethane, evaporating to dryness, followed by crystallization from pentane.

X-ray Diffraction

Green crystals of the compound, because of their extreme sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries in an argon-filled drybox. A crystal approximately 0.16 × 0.3 × 0.3 mm in size was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of several low-angle reflections showed half-peakwidths of 0.12–0.16°. The space group is *Pbca*. The setting angles of 12 manually centered reflections ($42° < 2\theta < 49°$) were used to determine by least squares the following cell parameters: a = 15.207 (4) Å, b = 12.021 (3) Å, c = 33.427 (9) Å. For Z = 8, V = 6110.6 $Å^3$, and a molecular weight of 719.84, the calculated density is 1.565 g cm^{-3}.

Intensity data of all the reflections indices $\pm h,+k,+l$ were collected with use of the θ–2θ scan technique with a scan speed of 2°/min in the range of $4° < 2\theta < 45°$. Each reflection was scanned 0.7° before $K\alpha_1$ peak, to 0.7° after the $K\alpha_2$ peak, and backgrounds were counted for 4 s at each end of the scan range. The temperature during data collection was 23 ± 1 °C. Three standard reflections were measured after every 250th scan to monitor for crystal decay, instrumental stability, and crystal alignment. A decay of 6% was observed in the intensities of the standards, and the data were adjusted accordingly. A total of 8749 scans (including standards) were performed, resulting in 4011 unique data of which 3025 had $I > \sigma(I)$. Correction for absorption (μ = 54 cm^{-1}) was made by an analytical integration method,[14] and the factors ranged from 2.7 to 4.1.

The three-dimensional Patterson calculations indicated the U atom positions, and subsequent least-squares refinements and Fourier calculations revealed the positions of the Si, N, O, and C atoms. Difference Fourier maps revealed some but not all of the hydrogen atoms. Hydrogen atoms of the bis[(trimethylsilyl)amide] groups were included in the least-squares refinements but restrained to positions of 0.95 ± 0.05 Å from adjacent carbon atoms in the manner suggested by Waser[15] and described in one of our previous papers.[16] Hydrogen atoms in the dimethoxyethane ligand were not included because of large thermal motions apparent on that portion of the structure. In the final refinements all of the nonhydrogen atoms were assigned anisotropic thermal parameters, and the hydrogen atoms were assigned one overall isotropic thermal parameter. Extinction effects were evident in the data and an empirical extinction correction of the type $F_{cor} = F_o(1 + kI)$ was applied where $k = 2.8 \times 10^{-7}$ (I is the raw intensity, F_o is the observed structure factor, and F_{cor} is the modified observed structure factor); the largest intensity was the 200 reflection, and its structure factor was increased by 18% by the extinction correction.

The full-matrix least-squares program minimizes the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ where the assigned weights $w = [\sigma(F)]^{-2}$ were derived from $\sigma(F^2) = [S^2 + pF^2]^{1/2}$ where S^2 is the variance due to counting statistics and p = 0.04. Scattering factors from Doyle and Turner[17] for nonhydrogen atoms and from the International Tables[18] for hydrogen were used, and anomalous dispersion corrections[19] were applied. The final R factors, $R = \sum||F_o| - |F_c||/\sum|F_o|$, were 0.037 for 353 parameters and 2525 data with $F^2 > 2\sigma(F^2)$ and 0.079 for all 4083 data. The weighted $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ was 0.035 and the estimated standard deviation of a reflection of unit weight was 1.05. In the last cycle no nonhydrogen atom parameter changed more than 0.15 σ. The largest peak in the difference Fourier was 1.2 e/$Å^3$ and is a ripple 1.03 Å from the uranium atom.

Positional parameters are given in Table I. Tables of the anisotropic thermal parameters and the list of observed structure factors are given in the supplementary material. Distances and angles are given in Tables II and III, with atom numbers as in Figure 1.

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Registry No. $[(Me_3Si)_2N]_2UCl_2\cdot DME$, 77029-30-2; $[(Me_3Si)_2N]_2UCl_2$, 77029-21-1; UCl_4, 10026-10-5.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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(14) Templeton, L. K.; Templeton, D. H.; Abstracts, American Crystallographic Association Proceedings (1973), Series 2, Vol. 1, p. 143.

(15) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

(16) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1858.

(17) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 390.

(18) Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 97.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.