Synthesis, Structure, and Reactivity of the Sterically Crowded Complex (C₅Me₄SiMe₃)₃U

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In Memory of Professor Herbert Schumann

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Abstract. The unusual chemistry obtainable from sterically crowded $(C_5R_5)_3M$ complexes has been explored with M = U and $(C_5Me_4SiMe_3)^{1-}$, a ligand that has independently provided unexpected uranium chemistry. $(C_5Me_4SiMe_3)_2UMe_2$ (1), is reduced by potassium to generate the "ate" salt $(C_5Me_4SiMe_3)_2UMe_2K$ (2), which reacts with [HNEt₃][BPh₄] to yield the cationic species [$(C_5Me_4SiMe_3)_2U$][BPh₄] (3). KC₅Me₄SiMe₃ reacts with 3 in benzene to form $(C_5Me_4SiMe_3)_3U$,

(4). The structure of 4 shows that the displacement of the methyl groups from the cyclopentadienyl ring planes, a useful indicator of steric crowding, is the largest ever observed in a $(C_5R_5)_3M$ complex. The reactivity of 4 is consistent with this structural indicator in that it engages in THF ring opening to form $(C_5Me_4SiMe_3)_2UO-[(CH_2)_4(C_5Me_4SiMe_3)](THF).$

Introduction

This paper explores the effects of combining the $(C_5Me_4SiMe_3)^{1-}$ ligand with steric crowding in a tris(peralkylcyclopentadienyl) uranium complex. Recent studies of the $(C_5Me_4SiMe_3)^{1-}$ ligand attached to uranium have led to unusual C–H activation reactivity as shown in Equation (1) [1]. Specifically, in contrast to $(C_5Me_5)_2UMe_2$ [2], which has a half-life of 16 h at 100 °C, $(C_5Me_4SiMe_3)_2UMe_2$ (1) undergoes two C–H bond activation reactions to form the bis(tethered alkyl) complex (η^5 - $C_5Me_4SiMe_2CH_2$ - κ , $C)_2U$.



The latter complex has become an effective platform to generate many new types of tethered uranium metallocenes, e.g. Equation (2) [1, 3].

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As part of the exploration of the uranium chemistry of the $(C_5Me_4SiMe_3)^{1-}$ ligand, the synthesis of the tris(ligand) complex $(C_5Me_4SiMe_3)_3U$ was pursued. Sterically crowded tris(peralkylcyclopentadienyl) complexes, $(C_5R_5)_3M$, have their own unusual chemistry in that the normally inert peralkylcyclopentadienyl ligand becomes activated to engage in reduction, insertion, ring-opening, substitution, and sigma bond metathesis reactivity [4]. Recently, it was also found that $(C_5Me_5)^{1-}$ could participate in C–H activation chemistry when the synthesis of an extremely crowded complex was attempted [Equation (3)] [5].



Because the $(C_5Me_4SiMe_3)^{1-}$ ligand has reactive C–H bonds, as indicated in Equation (1), it was possible that the reaction of KC₅Me₄SiMe₃ with $[(C_5Me_4SiMe_3)_2U][BPh_4]$ could lead to C–H activation rather than $(C_5Me_4SiMe_3)_3U$. On the other hand, $(C_5Me_4SiMe_3)_3La$ had been made in an analogous way without any complicating metalation [Equation (4)] [6].

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To explore these two synthetic options and to make uranium vs. lanthanum comparisons, the synthesis of $(C_5Me_4SiMe_3)_3U$ was examined. This has led to the most crowded $(C_5R_5)_3M$ complex structurally characterized to date. The reactivity of the complex was preliminarily examined to see if it would effect ring opening of THF, a reaction well characterized for lanthanides by Schumann and co-workers [7].

Experimental Section

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox. Schlenk, and vacuum-line techniques. All reactions were performed at room temperature unless otherwise noted. Solvents were dried by passage through columns containing Q-5 and 4A molecular sieves. [D₆]Benzene and [D₈]THF were dried with sodium-potassium alloy, degassed using three freeze-pump-thaw cycles, and vacuum transferred before use. (C₅Me₄SiMe₃)₂UMe₂ (1) [1], and [HNEt₃][BPh₄] [8] were prepared as previously reported. KC5Me4SiMe3 was prepared according to the procedure reported for KC5Me5 [9]. Potassium metal in oil was purchased from Aldrich, washed with hexanes to remove the oil, and dried under vacuum before use. NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer at 25 °C. Infrared spectra were recorded as KBr pellets with a Varian 1000 FT-IR spectrometer. Elemental analysis was performed with a Perkin-Elmer 2400 CHN analyzer.

Syntheses

(C₅Me₄SiMe₃)₂UMe₂K (2): An orange solution of 1 (240 mg, 0.36 mmol) in toluene (15 mL) was added to a vial of toluene (5 mL) that contained a smear of potassium metal (14 mg, 0.37 mmol). This mixture was allowed to stir for 4 d with periodic scraping (twice per day) of the potassium metal from the vial walls. The resulting green suspension was centrifuged and the soluble portion discarded. The solid was washed three times with toluene and dried under vacuum to yield **2** as a green-gray powder (200 mg, 80 %). ¹H NMR ($[D_8]$ THF): $\delta = -13.9$ (s, 12 H, C₅Me₄SiMe₃), -12.5 (s, 12 H, C₅Me₄SiMe₃), -3.92 (s, 18 H, C₅Me₄SiMe₃) ppm. Only the ring methyl and trimethylsilyl resonances were located in the ¹H NMR spectrum of this paramagnetic complex. IR: $\tilde{v} = 2949$ (s), 2899 (s), 1583 (w), 1444 (w), 1389 (w), 1319 (m), 1247 (s), 1127 (w), 1017 (w), 833 (vs), 749 (s) cm⁻¹. C₂₆H₄₈KSi₂U (693.96): calcd. C 44.88, H 6.95; found C 43.55, H 6.75. Repeated analysis of this compound gave incomplete combustion as is sometimes observed with f element complexes [3, 10]. The 1.86 H:C ratio found matches the 1.86 ratio calculated.

 $[(C_5Me_4SiMe_3)_2U][BPh_4]$ (3): [HNEt₃][BPh₄] (250 mg, 0.58 mmol) was added to a stirred green suspension of 2 (200 mg, 0.3 mmol) in benzene (15 mL). After 5 min, the solution began to turn dark brown and was allowed to stir for an additional 12 h. The solution was centrifuged to remove insoluble material, and the solvent was removed under vacuum to yield a tacky brown powder. This solid was dissolved in methylcyclohexane (15 mL) and centrifuged to remove insoluble material. The solvent was under vacuum removed to yield 3 as a brown

powder (246 mg, 90 %). ¹H NMR (C₆D₆): $\delta = -4.37$ (s, 18 H, C₅Me₄SiMe₃), 2.88 (s, 12 H, C₅Me₄SiMe₃), 6.56 (s, 12 H, C₅Me₄SiMe₃) ppm. Only the ring methyl and trimethylsilyl resonances were located in the ¹H NMR spectrum. **IR**: $\tilde{v} = 3052$ (s), 2953 (s), 2907 (s), 1591 (s), 1431 (s), 1317 (w), 1240 (vs), 1030 (w), 884 (w), 837 (vs), 747 (s), 701 (vs) cm⁻¹. C₄₈H₆₂BSi₂U (944.03): calcd. C 61.07, H 6.62; found C 57.87, H 5.97. Repeated analysis of this compound gave incomplete combustion as is sometimes observed with f element complexes [3, 10]. The 1.24 H:C ratio found is close to the 1.30 ratio calculated.

(C₅Me₄SiMe₃)₃U (4): In a glovebox free of coordinating solvents, KC₅Me₄SiMe₃ (150 mg, 0.63 mmol) was added to a stirred brown solution of **3** (390 mg, 0.42 mmol) in toluene (15 mL). After the brown solution was stirred for 12 h, it was centrifuged to remove insoluble material and the solvent was removed under vacuum to yield **4** as a brown microcrystalline solid (324 mg, 95 %). X-ray quality crystals of **4** were grown from a concentrated hexane solution at $-35 \,^{\circ}C$. ¹H NMR (C₆D₆): $\delta = -16.7$ (s, 27 H, C₅Me₄SiMe₃), -3.80 (s, 18 H, C₅Me₄SiMe₃), 14.6 (s, 18 H, C₅Me₄SiMe₃) ppm. IR: $\tilde{\nu} = 2952$ (s), 2899 (s), 2084 (w), 1429 (m), 1321 (m 1248s), 1207 (w), 1016 (m), 839 (vs), 753 (m), 748 (m), 717 (m) cm⁻¹. C₃₆H₆₃Si₃U (818.18): calcd. C 52.85, H 7.76; found C 52.91, H 7.56.

(C₅Me₄SiMe₃)₂UO[(CH₂)₄(C₅Me₄SiMe₃)](THF): In a glovebox containing coordinating solvents, excess THF (5 mL) was added to **4** (10 mg, 0.012 mmol) resulting in a green solution. The solvent was removed under vacuum yielding a tacky green solid. The ¹H NMR spectrum in C₆D₆ contained resonances expected for the THF ring opened product: $\delta = -8.18$ (s, 12 H, C₅Me₄SiMe₃), -7.00 (s, 18 H, C₅Me₄SiMe₃), -5.59 (s, 12 H, C₅Me₄SiMe₃), -0.028 (s, 9 H, SiMe₃), 1.82 (s, 6 H, C₅Me₄SiMe₃), 1.91 (s, 6 H, C₅Me₄SiMe₃), 2.00 (s, 2 H, CH₂), 2.36 (s, 2 H, CH₂), 2.83 (s, 2 H, CH₂), 3.32 (s, 2 H, CH₂), 4.38 (m, THF), 6.80 (m, THF) (half height line widths ranged from 2 to 300 Hz) ppm. Similarly, in a stoichiometric reaction, THF (2.1 µL, 0.026 mmol) was added to **4** (11 mg, 0.013 mmol) in C₆D₆ (1 mL). The ¹H NMR spectrum was recorded, which gave the same ¹H NMR spectroscopic data as above.

Crystallographic Data

CCDC-778886 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Supporting Information (see footnote on the first page of this article): X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_4SiMe_3)_3U$ (4). NMR spectra of the elemental analysis samples for 2 and 3.

Results and Discussion

Synthesis

The synthesis of $(C_5Me_4SiMe_3)_3U$ was pursued in analogy to the synthesis of $(C_5Me_5)_3U$ [11]. $(C_5Me_4SiMe_3)_2UMe_2$ (1), is reduced by potassium to make the U^{3+} "ate" salt, $(C_5Me_4SiMe_3)_2UMe_2K$ (2), as a green-gray solid [Equation (5)]. Complex 2 was characterized by NMR and IR spectroscopy and by elemental analysis.



Complex **2** is an example of a rather small class of trivalent uranium alkyl complexes [11, 12] and its formation via Equation (5) is directly analogous to the synthesis of $(C_5Me_5)_2UMe_2K$ [11]. The ¹H NMR spectrum of **2** contained only resonances for the ring methyl and trimethylsilyl groups, whereas resonances for the methyl groups directly attached to paramagnetic uranium were not located. Similarly, methyl resonances were not located in the spectrum of $(C_5Me_5)_2UMe_2K$ [11].

The reaction of **2** with two equiv. of $[HEt_3N][BPh_4]$ generates the U^{3+} cation $[(C_5Me_4SiMe_3)_2U][BPh_4]$, **3**, as a brown solid [Equation (6)].

-2CH ₄	
-KBPh₄	(6)
2 -2NEt ₃	3

Complex **3** was also characterized by NMR and IR spectroscopy and by elemental analysis. The synthesis of **3** via Equation (6) is directly analogous to the formation of $[(C_5Me_5)_2U][BPh_4]$, and the NMR spectra are also similar in that resonances for the $[BPh_4]^{1-}$ anion were not observed [11].

The reaction of **3** with $KC_5Me_4SiMe_3$, the analog of Equation (3) and Equation (4) above, leads to formation of the tris(cyclopentadienyl) product ($C_5Me_4SiMe_3$)₃U (4) as a brown solid [Equation (7)].



Complex **4** was characterized by NMR and IR spectroscopy and elemental analysis, and was definitively identified by Xray crystallography (Figure 1). The ¹H NMR spectrum contains a single set of ligand resonances at -16.7, -3.80, and 14.6 ppm with ratios of 27:18:18, indicating that the three $(C_5Me_4SiMe_3)^{1-}$ rings are equivalent in solution. Details on the X-ray data collection parameters are given in Table 1.

Structure of 4

Complex 4 is not isomorphous with $(C_5Me_4SiMe_3)_3La$ (5), which was crystallized with a molecule of toluene in the lattice [6]. Comparisons of complexes 4 and 5 as well as $(C_5Me_5)_3U$ [13] and $(C_5Me_5)_3La$ [6] are given in Table 2.

The deviations of the silicon and methyl carbon atoms from the cyclopentadienyl ring planes, the metric parameter that has been consistently used to evaluate steric crowding in



Figure 1. Thermal ellipsoid plot of $(C_5Me_4SiMe_3)_3U$ (4), drawn to the 50 % probability level with hydrogen atoms excluded for clarity.

Table 1. X-ray data collection parameters for (C₅Me₄SiMe₃)₃U (4).

Empirical formula	$C_{36}H_{63}Si_{3}U(4)$
Formula weight	818.16
Temperature /K	148(2)
Crystal system	triclinic
Space group	$P\overline{1}$
a /Å	10.2024(7)
b /Å	12.2156(8)
c /Å	15.9301(11)
α /°	81.4802(7)
β /°	73.9260(7)
γ /°	71.8350(7)
Volume /Å3	1808.5(2)
Ζ	2
$\rho_{\rm calcd.}$ /Mg·m ⁻³	1.502
μ / mm^{-1}	4.610
$R1^{a}$ [$I \ge 2.0\sigma(I)$]	0.0167
$wR2^{b}$ (all data)	0.0420
a) $R1 = \Sigma F_0 - F_c / \Sigma F_0 $, b) v	$wR2 = \left[\sum \left[w(F_{0}^{2} - F_{c}^{2})^{2}\right]/\sum \left[w(F_{0}^{2})^{2}\right]\right]^{1/2}$

 $(C_5Me_5)_3M$ complexes [14], are compared between 4 and 5 in Table 3.

Comparisons of the structures should take into account differences in radial size of the metals. The only Shannon radius given for U^{3+} is for hexacoordination [15]. Comparing this 1.025 Å value with the six coordinate radius of La^{3+} , 1.032 Å, suggests that the nonacoordinate radius of U^{3+} should be slightly smaller than that of La^{3+} . Despite this slight difference, the U-(C₅Me₅ ring centroid) distance in the pentamethylcyclopentadienyl analog, (C₅Me₅)₃U, is 2.581 Å, compared to 2.642 Å in (C₅Me₅)₃La, and each of the three crystallographi-

Table 2. Bond lengths /	'Å and angles /° for	$(C_5Me_4SiMe_3)_3U$ (4	(C_5Me_5) ₃ U	[13], (C ₅ Me ₄ SiMe ₃) ₃ La	. (5) [6], a	and $(C_5Me_5)_3La$ [6].
0	0		// < 5 5/5			

4		$(C_5Me_5)_3U$		5		(C ₅ Me ₅) ₃ La	
UC(1)	2.968(2)	UC(1)	2.940(4)	La–C(1)	3.029(2)	La–C(1)	2.975(3)
U-C(2)	2.926(2)	U-C(2)	2.840(3)	La-C(2)	2.962(2)	La-C(2)	2.896(2)
U-C(3)	2.939(2)	U-C(3)	2.813(3)	La-C(3)	2.941(2)	La-C(3)	2.873(2)
U-C(4)	2.903(2)	U–Cnt	2.581	La-C(4)	2.940(2)	La-Cnt	2.642
U-C(5)	2.905(2)	Cnt-U-Cnt	120.0	La-C(5)	2.957(2)	Cnt-La-Cnt	120.0
U-C(13)	2.947(2)			La-C(13)	3.018(2)		
U-C(14)	2.897(2)			La-C(14)	2.986(2)		
U-C(15)	2.853(2)			La-C(15)	2.923(2)		
U-C(16)	2.848(2)			La-C(16)	2.890(2)		
U-C(17)	2.861(2)			La-C(17)	2.906(2)		
U-C(25)	2.889(2)			La-C(25)	2.988(2)		
U-C(26)	2.886(2)			La-C(26)	2.952(2)		
U-C(27)	2.906(2)			La-C(27)	2.948(2)		
U-C(28)	2.916(2)			La-C(28)	2.925(2)		
U-C(29)	2.857(2)			La-C(29)	2.925(2)		
U-Cnt(1)	2.666			La-Cnt(1)	2.706		
U-Cnt(2)	2.615			La-Cnt(2)	2.685		
U-Cnt(3)	2.625			La–Cnt(3)	2.687		
U-C(24)	3.561			La-C(24)	3.42		
U-C(35)	3.830			La-C(35)	4.10		
Cnt(1)-U-Cnt(2)	120.8			Cnt(1)–La–Cnt(2)	120.3		
Cnt(1)-U-Cnt(3)	120.9			Cnt(1)-La- $Cnt(3)$	119.5		
Cnt(2)-U-Cnt(3)	118.0			Cnt(2)–La–Cnt(3)	119.7		
Max. methyl displace ment from ring (Å)	e- 0.563		0.51		0.542		0.501

Table 3. Deviations /Å from the C_5Me_4R plane of the α -C (or Si) for each alkyl or silyl substituent for $(C_5Me_4SiMe_3)_3U$ (4) and $(C_5Me_4SiMe_3)_3La$ (5).

(C ₅ Me ₄ SiMe ₃) ₃ U (4)	(C ₅ Me ₄ SiMe ₃) ₃ La (5)
0.563 [C6]	0.542 [C6]
0.270 [C7]	0.236 [C7]
0.454 [C8]	0.313 [C8]
0.319 [C9]	0.364 [C9]
0.694 [Si1]	0.498 [Si1]
0.477 [C18]	0.458 [C18]
0.238 [C19]	0.271 [C19]
0.278 [C20]	0.279 [C20]
0.395 [C21]	0.369 [C21]
-0.113 [Si2]	0.161 [Si2]
0.467 [C30]	0.447 [C30]
0.202 [C31]	0.190 [C31]
0.255 [C32]	0.342 [C32]
0.418 [C33]	0.308 [C33]
0.022 [Si3]	0.190 [Si3]

cally unique M–C(C₅Me₅) bonds is 0.035–0.060 Å shorter in the uranium complex. A similar result is found when comparing the structures of **4** and **5**. The 2.615, 2.625, and 2.666 Å U–(ring centroid) distances in **4** are all smaller than expected when compared to the 2.685, 2.687, and 2.706 Å La–(ring centroid) distances in **5**, Table 2. The M–C(C₅Me₄SiMe₃) bonds in **4** vs. **5** are shorter by a larger range, 0.023–0.072 Å, than the differences observed between (C₅Me₅)₃U and (C₅Me₅)₃La.

The overall structures of **4** and **5** are similar in that each contains a distorted trigonal planar arrangement of cyclopentadienyl ring centroids around the metal. The centroid–M–centroid angles in **4** (118.0°–120.9°, like the 119.5°–120.3° angles in **5**) are clustered close to 120° . The uranium atom in **4** is 0.184 Å out of the plane of the ring centroids compared to 0.111 Å for lanthanum in **5** [6]. Each structure is also arranged so that two of the three SiMe₃ groups have two methyl groups pointing away from the crowded center of the molecule such that the third methyl group of those SiMe₃ units points toward the pseudo C₃ axis perpendicular to the plane of the three ring centroids. In **4**, this involves methyl carbons C24 and C35, which are located 3.56 and 3.83 Å, respectively, from uranium (Figure 2). Both distances are within the sum of the van der Waals radii of a methyl group (2.0 Å) [16] and uranium (1.86 Å) [17]. The comparable distances in **5** are 3.42 and



Figure 2. View of 4 showing how C24 and C35 are oriented toward uranium, where U1···C24 is 3.561 Å and U1···C35 is 3.830 Å.

4.10 Å, i.e., only one of these distances is in the U···C range.

Complexes 4 and 5 are also similar in that the third SiMe₃ group cannot adopt this favorable arrangement and has two methyl groups pointed in toward the center of the molecule, C10 and C11 in 4, Figure 2. This "more crowded" SiMe₃ group has the largest displacement of a substituent atom from the cyclopentadienyl ring plane in 4, 0.694 Å for Si1. In 5, the silicon displacement is large (0.498 Å), but not as large as the 0.542 Å displacement of a methyl group on that ring. The silicon atom displacements from the ring plane for the other SiMe₃ groups, i.e. the ones with methyl groups oriented toward the metal, are much less for both 4 and 5. This has also been observed, in general, with $(C_5Me_4R)_3La$ complexes (R = Et,*i*Pr) [6]. In **4**, this is taken to an extreme such that Si2, attached to C17, actually has a negative displacement, i.e., it is bent toward and not away from the metal atom. This is the first example of negative displacement of an R group in a peralkyl $(C_5R_5)_3M$ complex.

Complexes 4 and 5 are also similar in that the methyl group with the largest displacement is found on the ring with the longest *M*–(ring centroid) distance. In 4, this 0.563 Å displacement for C6 is the largest ever observed in a $(C_5R_5)_3M$ complex. Previously, the 0.542 Å value in 5 and the 0.5475 Å distance in $(C_5Me_5)_3Y$ [4b] were the largest found. Displacements of 0.48 to 0.54 Å have been observed to give unusual reactivity to the $(C_5R_5)^{1-}$ rings in $(C_5R_5)_3M$ complexes [14].

Reactivity of 4

To test if the large methyl displacements in 4 would lead to reactivity typical of sterically crowded $(C_5R_5)_3M$ complexes, compound 4 was dissolved in THF. This reaction immediately produced a green solution, from which a green solid can be isolated that has the characteristic NMR spectrum of a THF ring open product [7], in this case $(C_5Me_4SiMe_3)_2UO [(CH_2)_4(C_5Me_4SiMe_3)]$ (THF) [Equation (8)]. To establish if the larger methyl displacement in 4 compared to $(C_5Me_5)_3U$ could lead to an increase in reactivity, 4 was also reacted with two equiv. of THF. It has been previously reported that $(C_5Me_5)_3U$ does not react with stoichiometric amounts of THF [18]. Since complex 4 does react with stoichiometric THF, it is more reactive than $(C_5Me_5)_3U$ in this regard.



Conclusions

The sequence of syntheses that takes $(C_5R_5)_2UMe_2$ to $(C_5R_5)_2UMe_2K$ to $[(C_5R_5)_2U][BPh_4]$ to $(C_5R_5)_3U$ for $(C_5R_5)^{1-} = (C_5Me_5)^{1-}$ is also applicable for $(C_5R_5)^{1-} = (C_5Me_4SiMe_3)^{1-}$. Hence, $(C_5Me_4SiMe_3)_3U$ (4) can be made without the complicating C–H bond activation of the SiMe₃ groups on the cyclopentadienyl rings. Complex 4 contains the largest displacement from the ring plane of a methyl substituent ever observed in a peralkyl $(C_5R_5)_3M$ complex and is more reactive with THF than its permethyl analog, $(C_5Me_5)_3U$. The structure of 4 also is the first example of a $(C_5R_5)_3M$ complex with a negative displacement of a ring substituent. Comparison of the structure of 4 and its lanthanum analog, $(C_5Me_4SiMe_3)_3La$ (5) shows that 4 has more agostic interaction within the sum of van der Waals radii limits and bond lengths shorter than would be expected by comparison of ionic radii. This could be used as evidence that uranium is more covalent than lanthanum.

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