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STRUCTURE OF
TRIS(TRIMETHYLSILYLCYCLOPENTADIENYL)
URANIUM(III), $[(CH_3)_3SiC_5H_4]_3U$

J. Brennan, R.A. Andersen, and A. Zalkin

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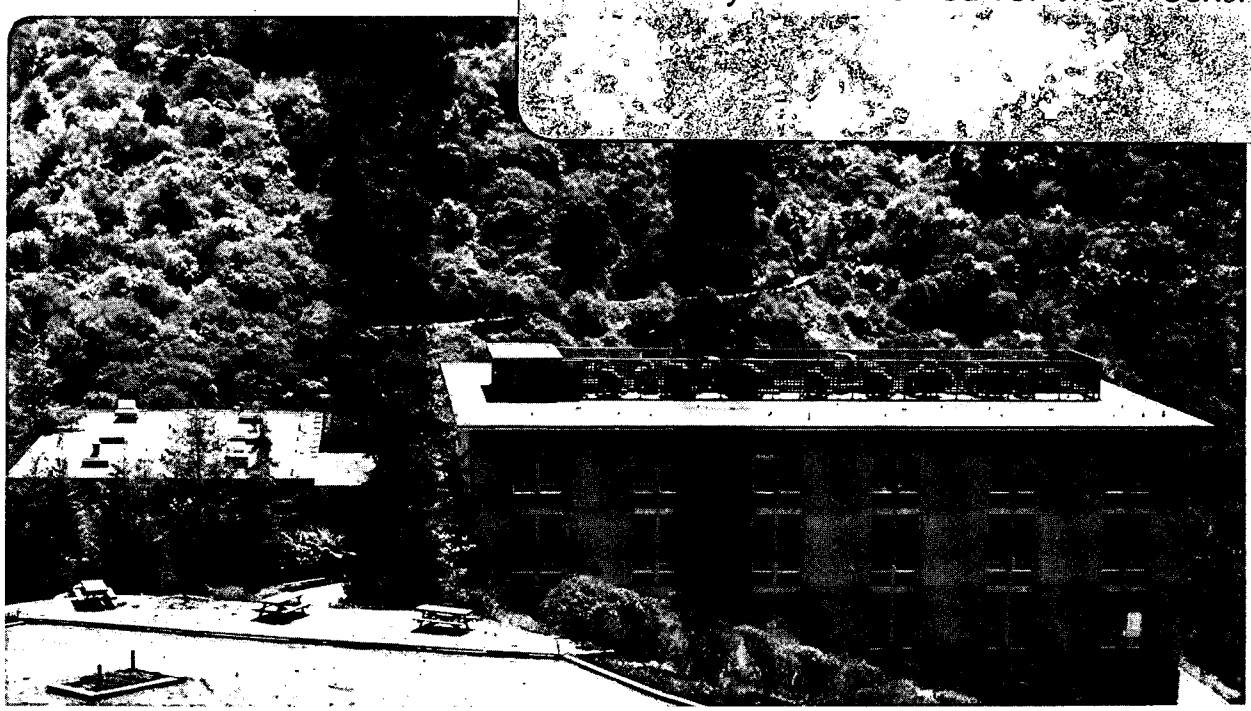

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Structure of Tris(trimethylsilylcyclopentadienyl)uranium(III), $[(CH_3)_3SiC_5H_4]_3U$

John Brennan, Richard A. Andersen, and Allan Zalkin

Crystals of $[(CH_3)_3SiC_5H_4]_3U$ are orthorhombic, Pbca, with a = 22.630(8), b = 29.177(10) and c = 8.428(3) A at 23 °C. For Z = 8 the calculated density is 1.551 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor of 0.041 [2251 data, $F^2 > 2\sigma(F^2)$]. The uranium atom is bonded to the three cyclopentadienyl rings in a pentahapto fashion and is in the plane of the ring centroids. The U to ring distances are 2.54, 2.47 and 2.51 A, and the average U-C distance is 2.78 ± 0.04 A.

Introduction. The title compound is one of several triscyclopentadienyl complexes of uranium(III) prepared for a study of their synthetic chemistry, structures and relative bascisities.[1]

Experimental. UCl_4 reacts with $K(Me_3SiC_5H_4)$ in tetrahydrofuran to give the red compound $(Me_3SiC_5H_4)_3UCl$ which when dissolved in hexane and stirred over Na/Hg or Na/K·yields the green compound $(Me_3SiC_5H_4)_3U(III)$.[8] The air-sensitive crystals were sealed inside quartz capillaries in an argon filled drybox. X-ray diffraction intensities (θ-2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer. The data were corrected for absorption (analytical method), crystal decay and Lorentz and polarization effects. Experimental details of the data collection are tabulated in Table I. The uranium atom position was deduced from three-dimensional Patterson maps, and subsequent least-squares refinements and electron density maps revealed the rest of the non-hydrogen atom positions. The structure was refined by full-matrix least-squares using anisotropic thermal parameters on all of the non-hydrogen atoms. Non-methyl hydrogen atoms were included in their estimated positions with fixed isotropic thermal paramters, but not refined; the methyl hydrogen atom positions could not be unambiguously estimated and were excluded. Atomic scattering factors and anomalous dispersion terms were taken from International Tables[2]. Statistical results and other details of the least-squares refinements are tabulated in Table I.

Results Atomic parameters are listed in Table II. A list of selected bonds and angles is given in Table III. Tables of anisotropic thermal parameters, hydrogen positions, least-square planes, and additional bond distances and bond angles are given in the supplementary material.

The titled compound is a monomolecular complex of uranium bonded to three trimethylsilylcyclopentadienyl ligands in a pentahapto fashion. The uranium atom lies in the plane of the three cyclopentadienyl centroids with Cp-U-Cp angles all close to 120° (Table III); the average U-C distance is 2.78 ± 0.04 Å (Table III). An ORTEP[3] schematic drawing of the structure is shown in Figure 1.

The U-Cp distances range from 2.48 to 2.54 Å and are comparable to the values found in the trimethylphosphine and thiophene coordination complexes of $(MeCp)_3U(III)$; for $(MeC_5H_4)_3U{\cdot}PMe_3$[4] and $(MeC_5H_4)_3U{\cdot}SC_4H_8$[5] the U-Cp distances range from 2.51-2.54 Å and 2.54-2.55 Å, respectively. These U(III)-Cp distances are remarkably similar to those in some U(V)-Cp and U(IV)-Cp complexes; i.e. in $(C_5H_5)_3U(V){=}CHP(CH_3)_2(C_6H_5)$[6] the U-Cp distance range is 2.49 to 2.55 Å; in $(C_5H_5)_3U(IV)(n\text{-}C_4H_9)$ and $(C_5H_5)_3U(IV)(CH_2C_6H_4Me)$[7] the U-Cp distance range 2.45 to 2.52 Å.

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References

1. Brennan, J. G. Ph.D. Thesis, Univ. of Calif. Berkeley, 1985, Lawrence Berkeley Laboratory Report No. 20845.

2. International Tables for X-ray Crstallography (1974). Vol. IV; Table 2.2, pp 71-102. Birmingham: Kynoch Press.

3. Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

4. Brennan, J. G.; Zalkin, A. Acta Crystallogr., 1985, C41, 1038-1040.

5. Zalkin, A:; Brennan, J. G. Acta Crystallogr., 1985, C41, 1295-1297.

6. Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. Organometallics, 1983, 2, 1336-1340.

7. Perego, G.; Cesari, M.; Farina,F.; Lugli, G. Gazz. Chim. Ital., 105, 643-646.

Table I. Crystallographic Summary and Data Processing for $[(CH_3)_3SiC_5H_4]_3U$

a, A[a]	22.630(8)
b, A	29.177(10)
c, A	8.428(3)
cryst syst	orthorhombic
space group	Pbca
volume, A^3	5564.8
d(calcd),g/cm^3	1.551
Z	8
temp (°C)	23
empirical formula	$C_{24}H_{39}Si_3U$
f(000)	2536
mol wt	649.87
x-ray	MoKα (graphite monochromated)
wave-length (Ka_1,Ka_2), A	0.70930,0.71359
crystal size (mm)	0.21 x 0.30 x 0.48
abs coeff, cm-1	56.64
abs corr range	2.99-4.82
cryst decay corr range	0.60-1.27
2θ limits, deg	4.6-50.1
hkl limits	h 0, 26; k 0, 34; ℓ -10, 10
scan type	θ-2θ
scan width, °2θ	1.20 + 0.693 × tanθ
no. of standards	3
no. reflections betwn stds	250
no. scan data	7595
no. unique reflections	4909

R_{int}[b]	0.054
no. non-zero weighted data	2251 ($F^2>2\sigma$)
p[c]	0.04
no. parameters	253
R (non-zero wtd dat)[d]	0.041
R_w[e]	0.041
R (all data)	0.147
Goodness-of fit[f]	1.22
max shift/esd in least-square	0.03
max,min in diff map (e/A^3)	1.78,-2.33

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved MoKα components of 29 reflections ($24° < 2\theta < 34°$).

[b] R_{int} = agreement factor between equivalent or multiply measured reflections = $\Sigma[I_{hkl} - \langle I_{hkl}\rangle] / \Sigma\langle I_{hkl}\rangle$

[c] In the least-squares, the assigned weights to the data are $1.0/[\sigma(F)]^2$ were derived from $\sigma(F^2) = [S^2 + (pF^2)^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.

[d] $R = \Sigma(|F_{obs}|-|F_{cal}|)/\Sigma|F_{obs}|$

[e] $R_w = \sqrt{[\Sigma w(|F_{obs}|-|F_{cal}|)^2/\Sigma w F_{obs}^2]}$

[f] σ_1 = error in observation of unit weight = $\sqrt{[\Sigma(w(|F_{obs}|-|F_{cal}|)^2)/(n_o-n_v)]}$, where n_o is the number of observations and n_v is the number of variables.

Table II. Positional Parameters with Estimated Standard Deviations[a]

for $[(CH_3)_3SiC_5H_4]_3U$

atom	x	y	z
U	0.22514(2)	0.12380(2)	0.08037(6)
Si(1)	0.10228(21)	0.02486(15)	0.2233(7)
Si(2)	0.37799(21)	0.17835(16)	0.2461(8)
Si(3)	0.08792(20)	0.14995(15)	-0.2207(7)
C(1)	0.1792(7)	0.0451(4)	0.2281(20)
C(2)	0.2263(10)	0.0286(5)	0.1363(19)
C(3)	0.2812(10)	0.0449(6)	0.1966(27)
C(4)	0.2641(12)	0.0707(7)	0.343(3)
C(5)	0.2042(10)	0.0718(6)	0.3510(22)
C(6)	0.2976(7)	0.1887(5)	0.2182(21)
C(7)	0.2505(9)	0.1824(7)	0.3197(25)
C(8)	0.1979(8)	0.2001(5)	0.2570(29)
C(9)	0.2125(9)	0.2171(5)	0.1063(23)
C(10)	0.2725(10)	0.2113(4)	0.0833(21)
C(11)	0.1650(6)	0.1312(5)	-0.2127(15)
C(12)	0.1860(9)	0.0845(5)	-0.2028(19)
C(13)	0.2479(9)	0.0854(7)	-0.2063(23)
C(14)	0.2694(7)	0.1310(6)	-0.2292(18)
C(15)	0.2162(7)	0.1582(5)	-0.2296(18)
C(16)	0.0477(8)	0.0747(6)	0.229(3)
C(17)	0.0902(9)	-0.0116(8)	0.408(3)
C(18)	0.0899(8)	-0.0123(6)	0.0435(28)
C(19)	0.4193(9)	0.2355(6)	0.237(3)
C(20)	0.4058(8)	0.1407(7)	0.078(3)
C(21)	0.3937(8)	0.1506(6)	0.4463(23)
C(22)	0.0349(7)	0.0989(5)	-0.242(3)
C(23)	0.0798(9)	0.1874(7)	-0.401(3)
C(24)	0.0642(9)	0.1863(7)	-0.044(3)

[a] Estimated standard deviations in this and subsequent tables are indicated in parentheses.

Table III: Bond Lengths and Angles for $[(CH_3)_3SiC_5H_4]_3U$

atoms	dist,A	atoms	dist,A
U - C(1)	2.811(14)	Si(1) - C(1)	1.839(16)
U - C(2)	2.816(14)	Si(1) - C(18)	1.885(21)
U - C(3)	2.806(17)	Si(1) - C(17)	1.905(24)
U - C(4)	2.843(21)	Si(1) - C(16)	1.909(15)
U - C(5)	2.780(17)	Si(2) - C(6)	1.860(16)
U - C(6)	2.761(14)	Si(2) - C(20)	1.900(23)
U - C(7)	2.706(20)	Si(2) - C(21)	1.905(19)
U - C(8)	2.748(17)	Si(2) - C(19)	1.914(15)
U - C(9)	2.746(16)	Si(3) - C(11)	1.829(14)
U - C(10)	2.768(13)	Si(3) - C(23)	1.882(21)
U - C(11)	2.828(13)	Si(3) - C(24)	1.903(23)
U - C(12)	2.792(15)	Si(3) - C(22)	1.920(14)
U - C(13)	2.713(18)	U - Cp(1)[a]	2.54
U - C(14)	2.802(16)	U - Cp(2)	2.48
U - C(15)	2.806(14)	U - Cp(3)	2.51

atoms	angle,°	atoms	angle,°
C(1) - SI(1) - C(16)	111.6(8)	C(20) - SI(2) - C(21)	110.7(9)
C(1) - SI(1) - C(17)	107.3(9)	C(11) - SI(3) - C(22)	111.6(7)
C(1) - SI(1) - C(18)	110.1(8)	C(11) - SI(3) - C(23)	107.2(8)
C(16) - SI(1) - C(17)	108.11(12)	C(11) - SI(3) - C(24)	114.0(9)
C(16) - SI(1) - C(18)	111.24(10)	C(22) - SI(3) - C(23)	108.38(10)
C(17) - SI(1) - C(18)	108.4(9)	C(22) - SI(3) - C(24)	109.10(10)
C(6) - SI(2) - C(19)	109.4(8)	C(23) - SI(3) - C(24)	106.27(10)
C(6) - SI(2) - C(20)	108.9(8)	Cp(1) - U - Cp(2)	120.2
C(6) - SI(2) - C(21)	111.3(9)	Cp(1) - U - Cp(3)	120.9
C(19) - SI(2) - C(20)	108.21(10)	Cp(2) - U - Cp(3)	118.0
C(19) - SI(2) - C(21)	108.25(10)		

[a] Cp(1), Cp(2) and Cp(3) are the centroids of atoms C(1)-C(5), C(6)-C(10) and C(11)-C(15) respectively.

Figure Caption

Fig. 1. ORTEP drawing of tris(trimethylsilylcyclopentadienyl)uranium(III); thermal ellipsoids at 50% probability level.

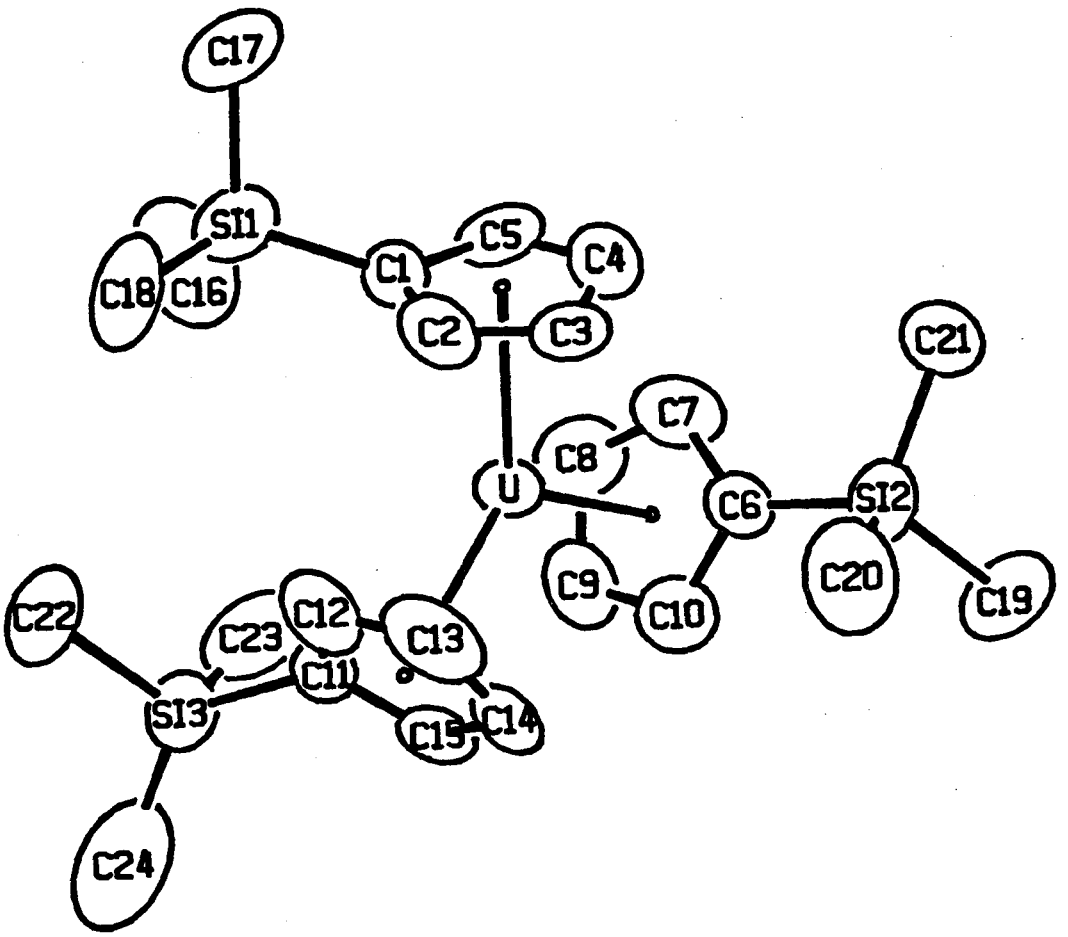
C17
SI1
C18
C16
C1
C5
C4
C2
C3
U
C8
C7
C6
SI2
C21
C20
C19
C9
C10
C22
C23
C12
C13
C11
SI3
C15
C14
C24

Fig. 1

Supplemental Material

Structure of Tris(trimethylsilylcyclopentadienyl)uranium(III), $[(CH_3)_3SiC_5H_4]_3U$

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Crystals of $[(CH_3)_3SiC_5H_4]_3U$ are orthorhombic, Pbca, with a = 22.630(8), b = 29.177(10) and c = 8.428(3) A at 23 °C. For Z = 8 the calculated density is 1.551 g/cm^3. The structure was refined by full-matrix least squares to a conventional R factor of 0.041 [2251 data, $F^2 > 2\sigma(F^2)$]. The uranium atom is bonded to the three cyclopentadienyl rings in a pentahapto fashion and is in the plane of the ring centroids. The U to ring distances are 2.54, 2.47 and 2.51 A, and the average U-C distance is 2.78 ± 0.04 A.

Table S1. Thermal Parameters[a] (A^2) with Estimated Standard Deviations for $[(CH_3)_3SiC_5H_4]_3$ U

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	4.713(23)	2.641(17)	3.046(19)	0.053(29)	0.08(3)	-0.044(27)
SI(1)	5.27(26)	5.39(23)	7.1(3)	0.04(19)	0.60(24)	1.66(24)
SI(2)	5.80(28)	6.18(25)	7.2(3)	-1.82(20)	-1.14(26)	0.40(26)
SI(3)	5.54(27)	4.95(21)	7.3(3)	-1.11(18)	-1.25(25)	1.14(23)
C(1)	5.6(9)	2.8(6)	4.0(8)	-1.0(6)	-1.0(8)	0.1(6)
C(2)	7.0(10)	3.0(6)	5.2(9)	0.3(9)	-1.5(11)	0.5(6)
C(3)	6.2(12)	6.6(10)	5.5(12)	-1.4(10)	-0.5(12)	3.3(9)
C(4)	7.9(15)	5.8(11)	9.3(17)	-2.0(12)	-4.4(15)	4.4(11)
C(5)	8.7(13)	4.9(8)	4.9(9)	-2.7(8)	1.4(9)	0.8(7)
C(6)	5.9(10)	4.0(7)	3.1(8)	-0.7(6)	-0.8(7)	-0.4(6)
C(7)	9.9(18)	5.7(12)	2.4(9)	-0.5(8)	1.0(8)	-1.6(8)
C(8)	7.2(12)	4.0(8)	6.5(12)	0.9(7)	0.6(11)	-0.2(8)
C(9)	6.5(12)	4.4(7)	5.6(11)	0.7(7)	-1.7(9)	-1.5(7)
C(10)	7.9(10)	3.0(6)	4.7(8)	-0.5(8)	-0.2(13)	-0.9(7)
C(11)	4.7(8)	4.9(8)	3.4(7)	-0.9(7)	-0.6(6)	0.0(6)
C(12)	7.9(12)	5.0(9)	4.8(10)	0.5(9)	-2.1(10)	-1.0(7)
C(13)	10.4(15)	5.9(11)	3.5(10)	2.6(9)	-1.0(8)	-1.8(8)
C(14)	6.1(9)	7.0(11)	3.2(6)	-0.7(10)	-1.8(8)	0.4(8)
C(15)	5.2(10)	5.2(8)	3.1(7)	0.3(7)	-0.6(7)	1.4(6)
C(16)	8.2(12)	10.2(12)	12.0(16)	5.5(10)	-2.7(13)	-3.0(14)
C(17)	8.1(12)	12.8(16)	11.0(16)	-3.8(11)	0.0(14)	5.9(15)
C(18)	6.7(11)	6.7(10)	11.3(18)	-2.9(8)	-0.5(11)	-2.9(11)
C(19)	12.9(16)	7.9(11)	9.3(13)	-6.5(10)	-0.4(14)	1.4(12)
C(20)	6.8(11)	11.3(14)	11.1(15)	1.1(10)	-0.9(13)	-1.5(14)
C(21)	8.3(11)	9.3(11)	6.5(12)	-2.2(9)	-2.6(10)	3.3(10)
C(22)	7.0(11)	6.1(8)	11.1(13)	-2.8(8)	-1.2(12)	0.7(11)
C(23)	7.6(12)	11.1(14)	17.9(23)	-1.5(10)	-3.2(14)	11.3(16)
C(24)	7.6(12)	9.5(13)	14.4(21)	-0.8(10)	3.2(13)	-4.5(14)
H(1) - H(12)	B = 10.0					

[a] The anisotropic temperature factor has the form:
$-0.25\exp(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \ldots)$.
The isotropic temperature factor has the form: $\exp -B(\sin\theta/\lambda)^2$.

Table S2. Estimated Hydrogen Positional Parameters in $[(CH_3)_3SiC_5H_4]_3U$

Atom		x	y	z
H(1)	C(2)	0.2219	0.0088	0.0433
H(2)	C(3)	0.3207	0.0399	0.1529
H(3)	C(4)	0.2917	0.0850	0.4180
H(4)	C(5)	0.1816	0.0885	0.4306
H(5)	C(7)	0.2537	0.1680	0.4243
H(6)	C(8)	0.1588	0.2000	0.3053
H(7)	C(9)	0.1852	0.2312	0.0303
H(8)	C(10)	0.2945	0.2213	-0.0115
H(9)	C(12)	0.1614	0.0568	-0.1947
H(10)	C(13)	0.2734	0.0586	-0.1939
H(11)	C(14)	0.3100	0.1415	-0.2406
H(12)	C(15)	0.2159	0.1915	-0.2410

Table S3. Additional Distance and Angles in $[(CH_3)_3SiC_5H_4]_3U$

atoms	d(A)	atoms	d(A)
C(1) - C(2)	1.402(23)	H(1) - C(2)	0.979
C(1) - C(5)	1.415(21)	H(2) - C(3)	0.978
C(2) - C(3)	1.425(26)	H(3) - C(4)	0.982
C(3) - C(4)	1.497(27)	H(4) - C(5)	0.972
C(4) - C(5)	1.358(28)	H(5) - C(7)	0.979
C(6) - C(7)	1.378(21)	H(6) - C(8)	0.974
C(6) - C(10)	1.431(21)	H(7) - C(9)	0.979
C(7) - C(8)	1.401(23)	H(8) - C(10)	0.986
C(8) - C(9)	1.403(26)	H(9) - C(12)	0.983
C(9) - C(10)	1.382(28)	H(10) - C(13)	0.978
C(11) - C(15)	1.409(17)	H(11) - C(14)	0.974
C(11) - C(12)	1.447(18)	H(12) - C(15)	0.976
C(12) - C(13)	1.401(21)		
C(13) - C(14)	1.429(23)		
C(14) - C(15)	1.441(19)		

atoms	angle(°)	atoms	angle(°)
SI(1) - C(1) - C(2)	126.7(13)	C(6) - C(7) - C(8)	112.0(19)
SI(1) - C(1) - C(5)	124.9(16)	C(7) - C(8) - C(9)	105.8(18)
C(1) - C(2) - C(3)	110.6(17)	C(8) - C(9) - C(10)	108.3(16)
C(2) - C(3) - C(4)	103.6(21)	C(6) - C(10)- C(9)	109.6(17)
C(3) - C(4) - C(5)	108.2(24)	C(12) - C(11)- C(15)	105.2(13)
C(1) - C(5) - C(4)	110.4(20)	C(11) - C(12)- C(13)	108.0(15)
SI(2) - C(6) - C(7)	131.0(14)	C(12) - C(13)- C(14)	111.2(15)
SI(2) - C(6) - C(10)	124.3(15)	C(13) - C(14)- C(15)	103.3(13)
C(7) - C(6) - C(10)	104.3(16)	C(11) - C(15)- C(14)	112.3(13)

Table S4. Least-squares Planes and Deviations from Least-squares planes in $[(CH_3)_3SiC_5H_4]_3U$

Equation of Plane #1. Atoms C(1) - C(5)

-1.17127 a + 23.95055 b - 4.79354 c = -0.22019

Deviations from Plane

atom	d(A)	atom	d(A)
C(1)	-0.003(22)	U	2.536(10)
C(2)	-0.012(28)	Si(1)	-0.375(33)
C(3)	0.023(30)		
C(4)	-0.041(35)		
C(5)	0.019(28)		

Equation of Plane #2. Atoms C(6) - C(10)

4.17998 a + 25.98811 b + 3.50068 = 6.91270

Deviations from Plane

atom	d(A)	atom	d(A)
C(6)	-0.001(23)	U	-2.473(09)
C(7)	-0.006(26)	SI(2)	0.164(33)
C(8)	0.014(30)		
C(9)	-0.010(25)		
C(10)	0.009(27)		

Equation of Plane #3. Atoms C(11) - C(15)

1.15662 a + 2.86370 b + 8.37624 + -1.22051

Deviations from Plane

atom	d(A)		
C(11)	0.006(18)	U	2.509(08)
C(12)	-0.021(24)	SI(3)	-0.097(27)
C(13)	0.024(25)		
C(14)	-0.012(23)		
C(15)	0.001(20)		

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