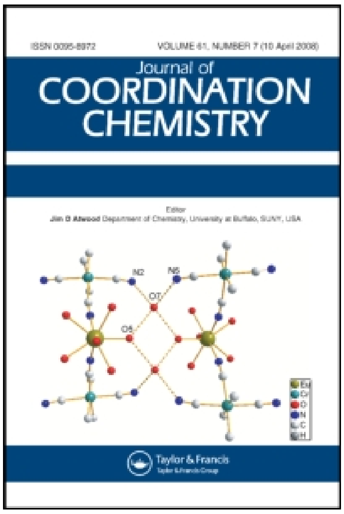

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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLOPENTADIENYLETHYNYLURANIUM(IV)

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INTRODUCTION

The history of the *sigma-bonded organometallic derivatives* of the *lanthanide* and *actinide* elements is in fact the history of the general organometallic chemistry of the metals. In 1938, Plets reported[2] the discovery of scandium and yttrium organometallics from the Grignard reactions:

$$MCl_3 + C_2H_5MgBr \xrightarrow[\text{reflux}]{(C_2H_5)_2O} \text{yellow oil}$$

$$M = Sc, Y$$

However, subsequent studies[3] have discounted this early claim.

The next substantial effort was the well-conceived attack on the problem by Gilman and Jones:[4]

$$La + C_6H_5I \xrightarrow[C_6H_6]{(C_2H_5)_2O \text{ or}} \text{N.R.}$$

$$La + (C_6H_5)_2Hg \xrightarrow[100d]{135°} \xrightarrow{C_6H_6 \text{ extract}} 15\% \text{ biphenyl}$$

$$LaCl_3 + C_6H_5Li \xrightarrow{(C_2H_5)_2O} \text{N.R.} \xrightarrow{C_6H_6} \text{black residue}$$

$$LaCl_3 + CH_3Li \xrightarrow{(C_2H_5)_2O} CH_4 + \text{dark syrup-like precipitate}$$

$$LaCl_3 + C_2H_5MgBr \xrightarrow{(C_2H_5)_2O} \text{N.R.}$$

In short, all the methods which had afforded sigma-bonded derivatives of the main group elements were tried without success. (After these disappointing results, it was 25 years before some of the same methods were used again.)

The first preparation of an *organolanthanide* or *actinide* was the tricyclopentadienyl series initiated by Wilkinson and coworkers[5,6] in 1956. Over the next 10 years, a wide variety of cyclopentadienyl derivatives were studied.[7–11] However, the only hints of a degree of sigma character in the metal–carbon bonds were provided by the X-ray crystal structure of $Sm(C_5H_5)_3$,[12,13] and by the nmr study of $Sm(C_9H_7)_3 \cdot THF$.[14]

In 1972, the preparation and structure of lithium tetrakis(2,6-dimethylphenyl)lutetiate,[15] and the general preparative schemes[16–18] for the formation of $(C_5H_5)_3UR$ set the direction for a very extensive chemistry of sigma-bonded organometallic derivatives:

$$(C_5H_5)_3UCl + RLi \xrightarrow{THF} (C_5H_5)_3UR + LiCl$$

A significant structural result[19] was obtained from the initial X-ray crystallographic investigation of $(C_5H_5)_3U[C{\equiv}CC_6H_5]$: the U–C(σ) bond length is 2.33(2) Å, while the U–C(η^5) separation is 2.68 Å: shorter than any value reported for a polyhapto ligand. This contraction has been borne out in subsequent structural investigations[20,21] (see Table I). The sigma bond lengths given for compounds **1** and **3** agree quite well when the correction of 0.08 Å for the change of carbon atom hybridization from sp to sp^3 is considered. Compounds **1** and **2** present lengths which are not significantly different when the associ-

TABLE I
Comparison of U–C sigma bond lengths

Compound	U–C(σ) bond length Å	Ref.
(1) $(C_5H_5)_3U[C{\equiv}CC_6H_5]$	2.33(2)	19
(2) $(C_5H_5)_3U[CH_3C(CH_2)_2]$	2.48(3)	20
(3) $(C_5H_5)_3U[n\text{–}C_4H_9]$	2.43(2)	21
(4) $(C_5H_5)_3U[CH_2\text{–}p\text{–}C_6H_4CH_3]$	2.54(2)	21

ated standard deviations are taken into account: 2.33(2) vs. 2.48(3) Å differ by 0.07 ± 0.036 Å ($\Delta = 1.9\sigma$) after the hybridization corrections.[22] One thus observes a consistent picture of sigma bond length contraction for $(C_5H_5)_3UR$.[23]

Since it has been suggested that the *U–C sigma bond* length in $(C_5H_5)_3U[C{\equiv}CC_6H_5]$ might be indicative of some multiple bond character, it was of interest to investigate the structure of $(C_5H_5)_3U$-$[C{\equiv}CH]$. Unfortunately, as will be discussed, crystallographic difficulties limited the accuracy of the observed bond lengths here as in the previous structures.[19-21]

EXPERIMENTAL SECTION

Single crystals of the dark green, air-sensitive compound were grown by slow evaporation of a toluene solution of $(C_5H_5)_3U[C{\equiv}CH]$ and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession (CuKα) photographs. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 reflections ($\theta > 8°$) accurately centred on the diffractometer are given in Table II. The space group is uniquely determined to be $P2_1/n$, an alternate setting of $P2_1/c[C^5_{2h}$; No. 14], from the systematic absences in $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = zn + 1$.

Although five sets of data have been taken on three different crystals, the procedure followed below corresponds to the set used in the final refinement. Data were taken on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the $\omega - 2\theta$ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the pre-scan ranged from 7 to 0.30° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation.

$$\text{scan range} = A + B \tan\theta$$

where $A = 0.70°$ and $B = 0.26°$. Aperture settings were determined in a like manner with $A = 4.0$ mm and $B = 0.87$ mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously.[13] As a check on the stability of the instrument and the crystal, three reflections, the (400), (020), and (004), were measured after every 25 reflections; the standards fluctuated within a range of ±3%.

TABLE II
Crystal data

Compound	$(C_5H_5)_3U[C{\equiv}CH]$
Mol wt	458.4
Linear abs coeff, cm^{-1}	137.6
Calcd density, g cm^{-3}	2.11
Max crystal dimensions, mm	0.04 x 0.17 x 0.67
Space group	$P2_1/n$
Molecules/unit cell	8
Cell constants,[a] Å	
a	18.047(9)
b	8.243(6)
c	19.428(9)
β	92.21(6)°
Cell vol, Å^3	2888

[a] MoKα radiation, λ0.71069Å. Ambient temperature of 23°.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1851 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 10 was obtained in the prescan. Based on these considerations, the data set of 1851 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects.[24] (The transmission factors ranged from 0.12 to 0.61.)

Full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[24] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for U and C were taken from Cromer and Waber;[25] those for H were from "International Tables for X-ray Crystallography."[26] The scattering for U was corrected for the real and imaginary components of anomalous dispersion using Cromer's table.[27]

SOLUTION AND REFINEMENT OF THE STRUCTURE

The existence of eight molecules per unit cell in the space group $P2_1/n$ implied that there are two molecules in the asymmetric unit. The positions of both independent uranium atoms were deduced by inspection of a Patterson map. (The R value for the uranium atoms alone was $R_1 = \Sigma \,|\, |F_o| - |F_c| \,| / \Sigma \,|F_o| = 0.14$.) A difference Fourier map phased on the uranium atoms clearly revealed the location of the cyclopentadienyl rings, but the resolution of individual carbon atom positions was poor. Nonetheless, placement of all carbon atoms followed by several cycles of least-squares refinement (with anisotropic thermal parameters for the uranium atoms and isotropic parameters for the carbon atoms) lowered the R factors to $R_1 = 0.074$ and $R_2 = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{1/2} = 0.083$. At this point the weighting scheme involved essentially unit weights except for a diminished contribution from the most intense reflections. Placement of the cyclopentadienyl hydrogen atoms in calculated positions led to final reliability indices of $R_1 = 0.072$ and $R_2 = 0.081$.

There were, however, two undesirable features of the refinement. First, the carbon–carbon bond

TABLE III
Final fractional coordinates and thermal parameters

Atom	x/a	y/b	z/c	B
U1	0.3562(1)	0.2958(2)	0.4127(1)	a
U2	0.5796(1)	0.8012(2)	0.1475(1)	b
1C1	0.2854(21)	0.5715(46)	0.3763(19)	4.7(8)
1C2	0.3396(22)	0.5733(48)	0.3416(20)	5.2(8)
1C3	0.4045(22)	0.6100(52)	0.3782(21)	5.5(8)
1C4	0.3847(19)	0.6124(44)	0.4436(18)	4.3(7)
1C5	0.3038(22)	0.5985(54)	0.4495(20)	5.9(9)
1C6	0.2977(27)	0.1530(59)	0.5178(25)	7.1(1.0)
1C7	0.3135(25)	0.2846(61)	0.5460(23)	6.8(9)
1C8	0.3959(24)	0.3064(61)	0.5448(23)	6.6(9)
1C9	0.4213(22)	0.1723(51)	0.5356(20)	5.6(8)
1C10	0.3609(27)	0.0618(60)	0.5144(24)	7.0(1.0)
1C11	0.3402(29)	0.2036(74)	0.2802(27)	8.6(1.2)
1C12	0.2723(17)	0.2342(37)	0.2959(16)	3.6(6)
1C13	0.2516(19)	0.1159(45)	0.3420(17)	4.3(6)
1C14	0.3133(22)	0.0008(49)	0.3504(20)	5.2(8)
1C15	0.3665(23)	0.0572(51)	0.3120(22)	5.8(9)
1C16	0.4844(22)	0.2735(49)	0.3925(20)	4.7(7)
1C17	0.5528(26)	0.2554(54)	0.3772(24)	6.2(9)
2C1	0.6189(21)	1.0988(50)	0.0861(19)	5.2(8)
2C2	0.5403(21)	1.1002(49)	0.1037(20)	5.1(8)
2C3	0.5331(38)	1.1097(84)	0.1679(37)	11.0(1.7)
2C4	0.6110(32)	1.0953(72)	0.2023(31)	8.6(1.4)
2C5	0.6396(25)	1.0934(58)	0.1601(25)	6.1(9)
2C6	0.6629(24)	0.5386(55)	0.1858(22)	6.6(9)
2C7	0.7090(25)	0.6275(60)	0.1550(23)	6.4(9)
2C8	0.7210(25)	0.7455(55)	0.1940(26)	6.4(9)
2C9	0.6923(26)	0.7572(58)	0.2444(26)	7.1(1.0)
2C10	0.6363(25)	0.6252(58)	0.2540(23)	6.7(9)
2C11	0.4797(21)	0.5542(47)	0.1247(20)	5.2(8)
2C12	0.4734(22)	0.5976(53)	0.1841(21)	5.6(9)
2C13	0.4376(24)	0.7445(54)	0.1846(23)	6.7(1.0)
2C14	0.4314(25)	0.7944(63)	0.1145(24)	7.2(1.0)
2C15	0.4590(19)	0.6711(44)	0.0746(18)	4.6(7)
2C16	0.6160[c]	0.7700	0.0340	5.0
2C17	0.6311(25)	0.7114(49)	−0.0232(23)	3.5(7)

[a] The uranium atoms were refined with anisotropic thermal parameters defined by

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

For U1, $\beta_{11} = 0.0024(1)$, $\beta_{22} = 0.0111(2)$, $\beta_{33} = 0.0030(1)$.
$\beta_{12} = 0.0005(1)$, $\beta_{13} = 0.0003(1)$, $\beta_{23} = -0.0006(1)$.

[b] For U2, $\beta_{11} = 0.0025(1)$, $\beta_{22} = 0.0111(2)$, $\beta_{33} = 0.0031(1)$
$\beta_{12} = 0.0001(1)$, $\beta_{13} = -0.0000(1)$, $\beta_{23} = -0.0003(1)$.

[c] The atomic parameters for 2C16 were not refined.

distances in the cyclopentadienyl rings varied greatly (see Table IV) from the expected values, and, second, one of the sigma bonded carbon atoms, 2C16, refined to a position much too close to its neighbor, 2C17. The first problem was dealt with by simply accepting the fact that in structures of this type the cyclopentadienyl bond lengths are often not chemically realistic.[20] The second problem was handled by freezing the position of 2C16 in the location derived from the difference Fourier map.

It should be noted that, since one of the major goals of the structure determination was the accurate definition of the U–C sigma bond, a total of five complete data sets on three different crystals were obtained. Refinement of each set individually, and refinement of a scaled combination of all five, produced in all cases a poorer[28] structure than that reported above. Likewise, other weighting schemes were applied, but to no avail. It is therefore believed that the model reported here is the best obtainable from this chemical system.

The largest parameter shifts in the final cycle of refinement were less than 0.30 of their estimated standard deviations. A final difference Fourier map showed several features of ~1.0 $e^-/Å^3$ around the cyclopentadienyl rings, but it was not possible to incorporate them into a meaningful model. The standard deviation of an observation of unit weight was 1.29. No systematic variation of $w(|F_o|-|F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table III.[29]

RESULTS AND DISCUSSION

The molecular structure of tricyclopentadienylethynyluranium (IV) and the atom numbering scheme are shown in Figure 1, while the important bond lengths and angles are listed in Tables IV and V. There are two crystallographically independent molecules in the asymmetric unit.

Of particular interest is the nature of the bond between the uranium atom and acetylide ligand. The U–C sigma bond length[30] is 2.36(3) Å, a value in substantial agreement with that reported for $(C_5H_5)_3U[C{\equiv}CC_6H_5]$ (Table I). The linear coordination of the acetylide ligand is shown by the U1–1C16–1C17 bond angle of 175(4)°.

Although there is a large spread in the U–C pi bond lengths, the average of the 30 independent values is 2.73(5) Å. From the tabulation of other structures involving U–C pi bonds (Table VI),

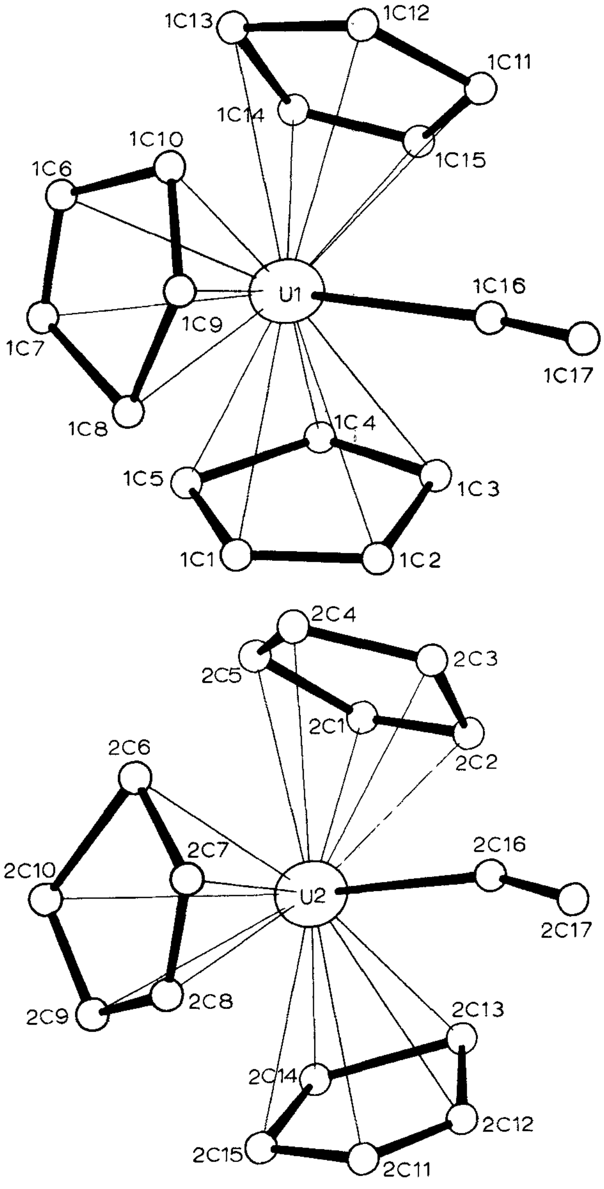

FIGURE 1 Molecular configuration and atom numbering scheme for $(C_5H_5)_3U[C{\equiv}CH]$.

2.73 Å appears to be the standard for cyclopentadienyl structures of this type. The two cyclooctatetraenyl compounds[31, 32] show significantly shorter π-bond lengths (2.65 → 2.66 Å), while the sterically hindered molecules, triindenylchlorouranium(IV),[35] and tetracyclopentadienyluranium(IV),[36] show significantly longer π-bond lengths (2.79 → 2.81 Å).

TABLE IV
Bond distances (Å) for $(C_5H_5)_3U[C\equiv CH]$

U1–1C16	2.36(3)	U2–2C16	2.33
U1–1C1	2.69(3)	U2–2C1	2.83(4)
U1–1C2	2.68(4)	U2–2C2	2.69(4)
U1–1C3	2.82(4)	U2–2C3	2.71(6)
U1–1C4	2.72(3)	U2–2C4	2.70(5)
U1–1C5	2.77(4)	U2–2C5	2.65(4)
U1–1C6	2.61(4)	U2–2C6	2.72(4)
U1–1C7	2.73(4)	U2–2C7	2.74(4)
U1–1C8	2.64(4)	U2–2C8	2.72(4)
U1–1C9	2.81(4)	U2–2C9	2.74(4)
U1–1C10	2.76(4)	U2–2C10	2.70(4)
U1–1C11	2.68(5)	U2–2C11	2.74(4)
U1–1C12	2.72(3)	U2–2C12	2.66(4)
U1–1C13	2.73(3)	U2–2C13	2.73(4)
U1–1C14	2.81(4)	U2–2C14	2.73(4)
U1–1C15	2.77(4)	U2–2C15	2.77(3)
U1–C(η^5)	2.73(6)	U2–C(η^5)	2.72(4)
1C16–1C17	1.29(5)	2C16–2C17	1.25
1C1–1C2	1.21(5)	2C1–2C2	1.47(5)
1C2–1C3	1.38(5)	2C2–2C3	1.26(7)
1C3–1C4	1.33(5)	2C3–2C4	1.54(7)
1C4–1C5	1.47(5)	2C4–2C5	0.99(6)
1C5–1C1	1.46(5)	2C5–2C1	1.47(5)
1C6–1C7	1.24(6)	2C6–2C7	1.23(6)
1C7–1C8	1.54(6)	2C7–2C8	1.25(6)
1C8–1C9	1.21(6)	2C8–2C9	1.13(6)
1C9–1C10	1.46(6)	2C9–2C10	1.50(6)
1C10–1C6	1.37(6)	2C10–2C6	1.59(6)
1C11–1C12	1.30(6)	2C11–2C12	1.22(5)
1C12–1C13	1.39(5)	2C12–2C13	1.37(6)
1C13–1C14	1.47(5)	2C13–2C14	1.42(6)
1C14–1C15	1.31(5)	2C14–2C15	1.38(6)
1C15–1C11	1.44(6)	2C15–2C11	1.41(5)
Cyclopentadienyl C–C average	1.37(13)	Cyclopentadienyl C–C average	1.35(13)

TABLE V
Bond angles (°) for $(C_5H_5)_3U[C\equiv CH]$

1C1–1C2–1C3	114[a]	2C1–2C2–2C3	112
1C2–1C3–1C4	104	2C2–2C3–2C4	107
1C3–1C4–1C5	112	2C3–2C4–2C5	98
1C4–1C5–1C1	97	2C4–2C5–2C1	134
1C5–1C1–1C2	112	2C5–2C1–2C2	89
1C6–1C7–1C8	108	2C6–2C7–2C8	105
1C7–1C8–1C9	106	2C7–2C8–2C9	121
1C8–1C9–1C10	109	2C8–2C9–2C10	112
1C9–1C10–1C6	105	2C9–2C10–2C6	90
1C10–1C6–1C7	109	2C10–2C6–2C7	111
1C11–1C12–1C13	107	2C11–2C12–2C13	109
1C12–1C13–1C14	108	2C12–2C13–2C14	106
1C13–1C14–1C15	106	2C13–2C14–2C15	108
1C14–1C15–1C11	108	2C14–2C15–2C11	102
1C15–1C11–1C12	111	2C15–2C11–2C12	115
U1–1C16–1C17	175	U2–2C16–2C17	161
1C16–U1–CENT1[b]	98	2C16–U2–CENT4	94
1C16–U1–CENT2	99	2C16–U2–CENT5	98
1C16–U1–CENT3	98	2C16–U2–CENT6	99
CENT1–U1–CENT2	116	CENT4–U2–CENT5	116
CENT1–U1–CENT3	117	CENT4–U2–CENT6	119
CENT2–U1–CENT3	121	CENT5–U2–CENT6	120

[a] The standard deviation in the bond angles is 4°.
[b] Centroids of the cyclopentadienyl rings defined such that

CENT1 = 1C1 → 1C5; CENT2 = 1C6 → 1C10;
CENT3 = 1C11 → 1C15; CENT4 = 2C1 → 2C5;
CENT5 = 2C6 → 2C10; CENT6 = 2C11 → 2C15.

TABLE VI
Comparison of U–C Pi bond lengths[a]

Compound	U–C mean π bond length (Å)	Ref.
$(C_8H_8)_2U$	2.65	31
$[(CH_3)_4C_8H_4]_2U$	2.66	32
$(C_5H_5)_3U[C\equiv CC_6H_5]$	2.68	19
$(C_5H_5)_3U[C\equiv CH]$	2.73	This study
$(C_6H_5CH_2C_5H_4)_3UCl$	2.73	33
$(C_5H_5)_3U[CH_3C(CH_2)_2]$	2.74	20
$(C_5H_5)_3UCl$	2.74	34
$(C_9H_7)_3UCl$	2.79	35
$(C_5H_5)_4U$	2.81	36

[a] All compounds contain uranium in the 4+ oxidation state.

The C(σ)- U–(center of ring angle of 98° is close to the corresponding value of 100° reported for $(C_5H_5)_3U[C\equiv CC_6H_5]$[19] and for $(C_5H_5)_3U[CH_3C(CH_2)_2]$.[20] Likewise, the (center of ring)–U–(center of ring) angle average of 118° agrees well with the 117° given for $(C_5H_5)_3U[C\equiv CC_6H_5]$ and for $(C_5H_5)_3U[CH_3C(CH_2)_2]$. The uranium atoms reside 2.47 Å out of the planes of the respective cyclopentadienyl rings (Table VII).

The C≡C bond lengths of 1.25 and 1.29(5) Å agree reasonably well with the 1.25(2) Å value obtained in $(C_5H_5)_3U[C\equiv CC_6H_5]$.[19] Within the cyclopentadienyl groups the wide range of C–C bond lengths (0.99 → 1.59 Å) is a manifestation of the crystallographic difficulties described in the Experimental Section. The average value of 1.36(13) Å represents evidence of the large librational motion of the cyclopentadienyl rings. Ideally, one would expect the C–C (cyclopentadienyl) bond length to be 1.43 Å,[37,38] and a contraction to 1.39 Å has recently been correlated to librational motion.[39] It is likely that the combination of such motion of the rings, together with the problem of the accurate location of light atoms in the presence of heavy ones, served to limit the overall accuracy of the structural determination.

TABLE VII
Least-squares planes for $(C_5H_5)_3U[C{\equiv}CH]$

Plane	Equation of plane
A	$-0.1264X + 0.9849Y - 0.1183Z - 3.1546 = 0$
B	$0.0711X + 0.3062Y - 0.9493Z + 8.8746 = 0$
C	$-0.3299X - 0.5387Y - 0.7752Z + 7.0618 = 0$
D	$-0.0498X - 0.9988Y - 0.0009Z + 9.5779 = 0$
E	$-0.7046X + 0.5071Y - 0.4964Z + 7.8308 = 0$
F	$-0.9040X - 0.4235Y - 0.0587Z + 9.8543 = 0$

Deviation of atoms from planes (Å)

Atom	Plane A	Atom	Plane B	Atom	Plane C
1C1	0.00	1C6	0.07	1C11	−0.02
1C2	−0.03	1C7	−0.10	1C12	0.02
1C3	0.04	1C8	0.09	1C13	−0.01
1C4	0.04	1C9	−0.05	1C14	0.00
1C5	0.02	1C10	−0.13	1C15	0.01
U1	−2.48	U1	2.45	U1	2.48
Atom	**Plane D**	**Atom**	**Plane E**	**Atom**	**Plane F**
2C1	−0.02	2C6	−0.04	2C11	0.04
2C2	0.04	2C7	0.03	2C12	−0.04
2C3	−0.03	2C8	0.01	2C13	0.03
2C4	0.02	2C9	−0.03	2C14	−0.01
2C5	0.00	2C10	0.04	2C15	−0.01
U2	2.46	U2	2.47	U2	−2.47

The unit cell packing, given as Figure 2, shows no unusually short intermolecular contacts.

In conclusion, the U–C sigma bond length is now known with certainty to be far shorter than the pi bond lengths. It must be noted, however, that this effect is not restricted to the inner transition metals. Sigma bond contraction has recently been reported among representative[40] and early transition metal compounds.[41,42] It seems reasonable to assume that the explanation of this observation for organouranium compounds will be found in a combination of the several ideas suggested thus far: orbital energy considerations,[42] ionic character of the sigma bond,[21] and the presence of multiple bonding in the acetylide linkage.[20]

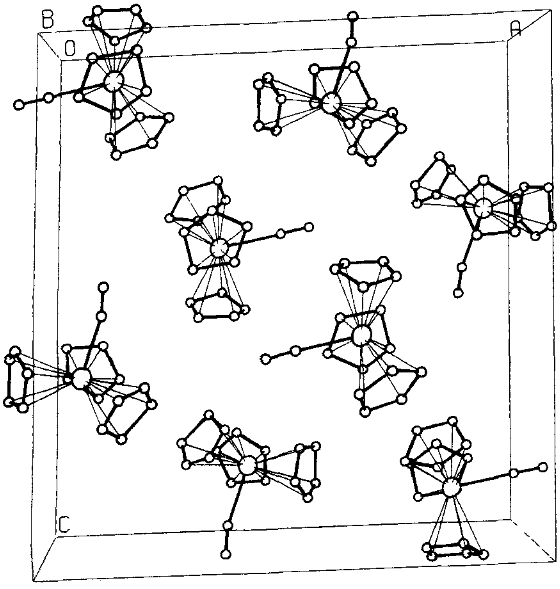

FIGURE 2 Unit cell packing diagram for $(C_5H_5)_3U[C{\equiv}CH]$.

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22. Using the relation $\sigma(\text{difference}) = (\sigma_1^2 + \sigma_2^2)^{1/2}$.
23. A similar, although not so pronounced, contraction is noted for the Lu–C bonds in lithium tetrakis(2,6-dimethylphenyl)lutetiate: the observed values are approximately 0.2 Å shorter than that calculated for a Lu–C(η^5) bond length.
24. Other crystallographic programs used on either an RCA 70/6 or a UNIVAC 1110 include ORFFE (distance and angles with esd's, by W. R. Busing, K. O. Martin, and H. A. Levy), ALFF (Fourier synthesis, by C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson), ORABS (absorption corrections, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and BPL (least-squares planes, by W. E. Hunter).
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28. The term "poorer structure" means that the derived bond distances and angles made poorer chemical sense than the structure reported herein.
29. The final values of the observed and calculated structure factor amplitudes are given in a table which may be obtained from the Editor's office.
30. Although there are two crystallographically independent molecules in the asymmetric unit, it was not possible to refine the carbon atom (2C16) bonded in sigma fashion to U2. Therefore, all subsequent discussion of the U–C sigma bond will refer to the parameters obtained for the molecule containing U1. It may be noted in Tables IV and V that the less accurately determined sigma bond parameters for U2 are nevertheless in good agreement with those for U1.
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