

Metal–Carbon σ -Bond in Organometallic Complexes of Uranium. The Crystal and Molecular Structures of $U(C_5H_5)_3(p\text{-CH}_3C_6H_4CH_2)$ and $U(C_5H_5)_3(n\text{-C}_4H_9)^*$

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The crystal and molecular structures of tricyclopentadienyl(*p*-methylbenzyl)uranium, $U(C_5H_5)_3(p\text{-CH}_3C_6H_4CH_2)$: orthorhombic, $a=19.64$ (2), $b=11.81$ (1), $c=8.19$ (1) Å, *Pnma*, $Z=4$, 1148 independent reflexions, four-circle diffractometer data, $R=0.041$, full-matrix refinement, and tricyclopentadienyl(*n*-butyl)uranium, $U(C_5H_5)_3(n\text{-C}_4H_9)$: orthorhombic, $a=8.64$ (1), $b=22.69$ (2), $c=8.66$ (1) Å, $P2_12_12_1$, $Z=4$, 1290 independent reflexions, four-circle diffractometer data, $R=0.049$, full-matrix refinement, have been determined by X-ray analysis. The two complexes display very similar geometries: the π -bonded cyclopentadienyl rings and the σ -bonded *p*-methylbenzyl (or *n*-butyl) groups are arranged tetrahedrally around the metal atom. The U–C σ -bond distances are 2.541 (15) Å in $U(C_5H_5)_3(p\text{-CH}_3C_6H_4CH_2)$ and 2.426 (23) Å in $U(C_5H_5)_3(n\text{-C}_4H_9)$. Some geometrical parameters of the σ -bonded ligands are quite unusual, and suggest an uncommon type of metal–carbon σ -bond: the U–C(σ -bonded)–C angles are about 128° in the two complexes, while the $C_\alpha\text{--}C_\beta\text{--}C_\gamma$ and $C_\beta\text{--}C_\gamma\text{--}C_\delta$ bond angles in the butyl ligand are 123.3 (13) and 116.3 (12)° respectively.

Introduction

Considerable interest is now being shown in the organometallic chemistry of actinides, and particularly in complexes containing a metal–carbon σ -bond. Some papers concerning the synthesis and spectroscopy of a series of organometallic complexes of U, with the general formula $U(C_5H_5)_3R$, have been published (Brandi, Brunelli, Lugli, Palladino, Pedretti & Salvatori, 1970; Brandi, Brunelli, Lugli & Mazzei, 1973; Calderazzo, 1972, 1973; Gebala & Tsutsui, 1973; Marks, Seyam & Kolb, 1973); in these complexes some of the protons of the σ -bonded alkyl or aryl groups show very large chemical shifts, as evidenced by 1H NMR measurements (Brandi *et al.*, 1973; Marks, Seyam & Kolb, 1973). The amount of X-ray structural data at present available for this class of complexes is small even though the σ -bonded nature of the R group has been confirmed in the case of $U(C_5H_5)_3(C_2C_6H_5)$ (Atwood, Hains, Tsutsui & Gebala, 1973) and $U(C_5H_5)_3[CH_3C(CH_2)_2]$ (Raymond, 1974). Therefore the determination of the crystal structures of tricyclopentadienyl(*p*-methylbenzyl)uranium, $U(C_5H_5)_3(p\text{-CH}_3C_6H_4CH_2)$, (I), and tricyclopentadienyl(*n*-butyl)uranium, $U(C_5H_5)_3(n\text{-C}_4H_9)$, (II), was undertaken. A preliminary communication concerning these two crystal structures has appeared (Perego, Cesari, Farina & Lugli, 1975); in this paper we report the details of the complete structure analysis.

Experimental

Crystals of both compounds were sealed in thin-walled glass capillaries under a dry nitrogen atmosphere. The space group and preliminary lattice constants were determined from Weissenberg photographs. From the systematic absences the space groups *Pn*2₁*a* or *Pnma* were assigned for (I); the latter was subsequently confirmed by successful refinement. The space group *P*2₁2₁2₁ was unambiguously assigned for (II). The unit-cell parameters were refined by a least-squares fit to the setting angles measured for 24 and 27 reflexions [(I) and (II) respectively] on the diffractometer. The crystal data are summarized in Table 1.

Data collection

Complex (I): The crystal selected for data collection was prismatic and bounded by the following eight planes: (100), (220), ($\bar{1}00$), ($\bar{4}10$), ($\bar{4}30$), (355), ($\bar{2}2\bar{3}$), ($\bar{1}11$). The maximum crystal dimensions were approximately 0.3 × 0.15 × 0.4 mm. The crystal was mounted with the *c* axis along the spindle axis of an on-line Siemens AED diffractometer; Zr-filtered Mo $K\alpha$ radiation was used. A total of 1942 reflexions were measured [maximum $(\sin \theta)/\lambda = 0.62 \text{ \AA}^{-1}$] with the θ - 2θ scan method and the 'five-points' technique (Hoppe, 1969). 1148 reflexions with intensities greater than $2.5\sigma(I)$, where $\sigma^2(I) = \text{total count} + (0.005I)^2$, were used for the structure determination. A standard reflexion, measured every 15 reflexions, monitored the intensity fluctuations, which did not exceed 3%. The intensities were then corrected by means of a simple linear interpolation method and were reduced to values of F^2 by applying Lorentz and polarization factors. The ab-

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sorption correction was applied according to the method proposed by Busing & Levy (1957).

Complex (II): A crystal with maximum dimensions of $0.3 \times 0.03 \times 0.55$ mm was chosen for data collection. Its irregular shape was defined by means of the following boundary planes: (103), ($\bar{1}01$), ($\bar{1}0\bar{1}$), ($\bar{2}0\bar{3}$), (100), (010), (0 $\bar{1}0$). The crystal was mounted with the [201] axis nearly parallel to the axis of the diffractometer. The apparatus and the procedure used for the collection of the intensities have been described above for (I).

The 3489 reflexions collected, corresponding to two octants of the sphere [maximum $(\sin \theta)/\lambda = 0.62 \text{ \AA}^{-1}$], included the hkl and $hk\bar{l}$ sets. A correction, based on a simple linear interpolation method, was applied for

intensity decay monitored by a standard reflexion; the maximum long-term variation was about 10%. The intensities were corrected for Lorentz and polarization effects; the absorption correction was applied, with the same procedure as for (I). The calculated absorption correction factors were systematically larger for one set of hkl reflexions than for the other, depending on the pronounced anisotropy of the crystal used. Even though the agreement between the intensities of hkl and $hk\bar{l}$ pairs was fairly good after the correction was applied, some small but systematic discrepancies were observed between the two sets; for this reason the set of data corresponding to the smaller absorption was chosen. 1290 independent reflexions with intensities

Table 1. Summary of crystal data

	(I)	(II)
Molecular formula	$U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$	$U(C_5H_5)_3(n-C_4H_9)$
Molecular weight	538.5	490.4
Space group	$Pnma$	$P2_12_12_1$
Molecules/unit cell	4	4
Calculated density (g cm^{-3})	1.882	1.918
a (\AA)*	19.64 (2)	8.64 (1)
b	11.81 (1)	22.69 (2)
c	8.19 (1)	8.66 (1)
Cell volume (\AA^3)	1899.6	1697.7
μ (cm^{-1})	128.0	143.0

* $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$.

Table 2. Atomic fractional coordinates and thermal parameters of non-hydrogen atoms

Anisotropic thermal factor defined by: $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)]$. Standard deviations in parentheses, in this and following tables, refer to the last digit quoted.

 $U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0.14434 (2)	$\frac{1}{4}$	-0.00567 (4)	3.15 (2)	2.90 (2)	1.71 (2)		-0.46 (5)	
C(1)	0.0168 (8)	$\frac{1}{4}$	0.0445 (21)	2.5 (5)	13.4 (17)	3.8 (7)		-1.2 (10)	
C(2)	-0.0192 (9)	$\frac{1}{4}$	0.1989 (17)	3.8 (7)	7.9 (11)	2.9 (6)		-0.4 (11)	
C(3)	-0.0371 (7)	0.3520 (11)	0.2793 (16)	5.3 (6)	6.7 (7)	5.9 (6)	4.8 (12)	0.9 (11)	4.2 (11)
C(4)	-0.0682 (6)	0.3498 (10)	0.4283 (14)	4.4 (5)	6.3 (6)	4.3 (5)	3.5 (11)	1.1 (9)	1.1 (9)
C(5)	-0.0850 (7)	$\frac{1}{4}$	0.5083 (20)	3.2 (5)	5.1 (7)	5.3 (8)		-2.4 (14)	
C(6)	-0.1220 (11)	$\frac{1}{4}$	0.6746 (22)	5.9 (9)	6.6 (10)	5.5 (8)		4.5 (15)	
C(7)	0.1251 (9)	0.4606 (13)	0.1193 (31)	7.6 (9)	4.8 (7)	12.6 (13)	-0.8 (14)	1.7 (20)	-9.8 (17)
C(8)	0.1457 (14)	0.4006 (13)	0.2402 (15)	23.8 (22)	5.6 (7)	2.1 (4)	-8.5 (21)	9.7 (17)	-4.3 (9)
C(9)	0.2142 (12)	0.3796 (11)	0.2034 (28)	10.8 (10)	3.2 (10)	11.5 (10)	-2.6 (19)	-7.6 (18)	-5.7 (16)
C(10)	0.2239 (8)	0.4343 (14)	0.0565 (22)	6.0 (7)	7.7 (8)	9.7 (10)	-10.6 (14)	4.8 (14)	-8.5 (15)
C(11)	0.1646 (10)	0.4786 (12)	0.0010 (15)	9.9 (10)	5.2 (6)	4.3 (6)	-1.5 (14)	-2.4 (15)	-0.2 (9)
C(12)	0.0809 (9)	$\frac{1}{4}$	-0.3070 (15)	4.2 (14)	16.2 (12)	0.6 (12)		-1.6 (18)	
C(13)	0.1259 (12)	0.3390 (14)	-0.3105 (13)	16.3 (16)	6.7 (8)	2.4 (4)	8.6 (19)	-1.7 (13)	1.9 (9)
C(14)	0.1947 (8)	0.3071 (11)	-0.3074 (12)	7.1 (8)	6.4 (7)	3.4 (5)	-5.4 (12)	-0.9 (10)	2.6 (8)

 $U(C_5H_5)_3(n-C_4H_9)$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0.03444 (8)	0.10715 (3)	-0.10882 (8)	3.33 (2)	3.57 (2)	4.62 (2)	0.05 (6)	-0.30 (6)	0.14 (6)

	x	y	z	B	x	y	z	B	
C(1)	-0.1219 (27)	0.1698 (10)	-0.2737 (25)	6.1 (5)	C(11)	0.1166 (48)	0.0755 (17)	-0.3913 (46)	11.8 (9)
C(2)	-0.2478 (32)	0.1530 (12)	-0.3759 (34)	8.0 (6)	C(12)	0.2575 (49)	0.0758 (17)	-0.3110 (48)	11.4 (10)
C(3)	-0.3229 (38)	0.1944 (14)	-0.4844 (38)	9.0 (7)	C(13)	0.2572 (45)	0.0311 (15)	-0.2211 (40)	10.3 (8)
C(4)	-0.4543 (36)	0.1701 (12)	-0.5785 (30)	8.7 (6)	C(14)	0.1409 (34)	0.0007 (12)	-0.2232 (32)	7.7 (6)
C(5)	-0.2228 (31)	0.0395 (12)	-0.0611 (28)	7.1 (6)	C(15)	0.2974 (31)	0.1499 (11)	0.0311 (30)	7.3 (5)
C(6)	-0.2585 (30)	0.0957 (11)	-0.0016 (30)	7.5 (5)	C(16)	0.1969 (35)	0.1615 (13)	0.1354 (34)	8.2 (7)
C(7)	-0.1887 (34)	0.1120 (14)	0.1143 (37)	9.6 (6)	C(17)	0.0946 (43)	0.2009 (15)	0.0751 (41)	10.9 (9)
C(8)	-0.0875 (30)	0.0622 (11)	0.1551 (28)	7.2 (5)	C(18)	0.1576 (41)	0.2146 (15)	-0.0600 (40)	10.0 (9)
C(9)	-0.1216 (32)	0.0209 (12)	0.0509 (29)	7.2 (6)	C(19)	0.2769 (47)	0.1831 (19)	-0.1004 (50)	12.4 (9)
C(10)	0.0389 (42)	0.0233 (14)	-0.3393 (36)	9.8 (8)					

greater than $2.5\sigma(I)$, where $\sigma^2(I) = \text{total count} + (0.005I)^2$, were used for the structure determination.

Structure determination and refinement

Both structures were solved by the application of heavy-atom techniques. Full-matrix least-squares refinements on F were used in which the function minimized was $\sum w(F_o - F_c)^2$; Cruickshank's (1965) weighting scheme was used.

Attempts to locate H atoms from ΔF maps were unsuccessful; therefore the usual planar or tetrahedral geometry and a C-H bond length of 1.0 Å were assumed and the positions calculated; the H atoms of the methyl group in (I), the positions of which cannot be unequivocally assigned, have been neglected. The contributions of the H atoms were included in the calculation of the structure factors and kept fixed during the refinement; isotropic temperature factors of 8.0 and 10.0 Å² were assumed for (I) and (II) respectively. Neutral scattering factors for U and C atoms were taken from Cromer & Mann (1968), while those of H were from Stewart, Davidson & Simpson (1965). The calculations included both $\Delta f'$ and $\Delta f''$ corrections for the anomalous dispersion effects of the U atom (Cromer, 1965). All the computer programs were written by Immirzi (1967, 1973). In the structure of (I), the U atoms form a pseudo- B -centred cell within the true cell so that the coordinates of the metal atom, determined from the Patterson map, phased only the reflexions for which $h + l = 2n$. In spite of the higher symmetry of the Fourier map so calculated, the positions of the C atoms of the p -methylbenzyl group were assigned, and this allowed all the reflexions to be phased. The subsequent Fourier map revealed the locations of all the other C atoms and gave strong evidence for a symmetry plane, suggesting $Pnma$ as the correct space group. Refinements carried out for both $Pn2_1a$ and $Pnma$ indicated that the former should be definitely rejected. After the anisotropic refinement of all non-hydrogen atoms, R dropped to 0.041. The coordinates of the metal atom in (II) were determined from a three-dimensional Patterson map. The positions of the 19 C atoms of the molecule were deduced from a subsequent Fourier synthesis.

The necessarily approximate absorption correction (because of the irregular shape of the crystal) affected the thermal parameters of the C atoms which were left isotropic; only the U atom was refined anisotropically. The final R was 0.049. The enantiomorphous structure, whose refinement gave a final R of 0.051, was rejected, even though the small difference between the R values could not be a sufficiently reliable test of the absolute configuration. However, the differences between the atomic parameters of the enantiomorphous structures at the end of the refinement were negligible.

For (I) a final difference Fourier synthesis showed no peaks greater than 0.7 e Å⁻³ beyond 1.7 Å of the U atom; for (II) some peaks below 1.5 e Å⁻³,

within 3 Å of the metal atom, could be justified by the isotropic refinement of the C atoms.

The final positional and thermal parameters of the non-hydrogen atoms of (I) and (II) are reported in Table 2. The calculated H positions for the two complexes are listed in Table 3.*

Table 3. *Calculated positions of the H atoms*

U(C ₅ H ₅) ₃ (p -CH ₃ C ₆ H ₄ CH ₂)			
	x	y	z
H(C1)	-0.0002	0.3189	-0.0136
H(C3)	-0.0302	0.4274	0.2203
H(C4)	-0.0767	0.4201	0.4898
H(C7)	0.0762	0.4863	0.1043
H(C8)	0.1165	0.3871	0.3336
H(C9)	0.2497	0.3372	0.2720
H(C10)	0.2694	0.4362	-0.0051
H(C11)	0.1569	0.5180	-0.1088
H(C12)	0.0329	$\frac{1}{2}$	-0.3211
H(C13)	0.1155	0.4230	-0.3057
H(C14)	0.2355	0.3553	-0.3129
U(C ₅ H ₅) ₃ (n -C ₄ H ₉)			
	x	y	z
H'(C1)	-0.0456	0.1901	-0.3421
H''(C1)	-0.1686	0.1994	-0.2019
H'(C2)	-0.3340	0.1352	-0.3068
H''(C2)	-0.2207	0.1161	-0.4333
H'(C3)	-0.2444	0.2097	-0.5528
H''(C3)	-0.3653	0.2278	-0.4234
H'(C4)	-0.4918	0.2018	-0.6456
H''(C4)	-0.4114	0.1366	-0.6416
H'''(C4)	-0.5359	0.1553	-0.5085
H(C5)	-0.2534	0.0214	-0.1613
H(C6)	-0.3392	0.1214	-0.0486
H(C7)	-0.1946	0.1520	0.1685
H(C8)	-0.0100	0.0616	0.2402
H(C9)	-0.0797	-0.0199	0.0567
H(C10)	-0.0639	0.0066	-0.3692
H(C11)	0.0847	0.1077	-0.4647
H(C12)	0.3449	0.1061	-0.3223
H(C13)	0.3474	0.0219	-0.1456
H(C14)	0.1234	-0.0341	-0.1583
H(C15)	0.3816	0.1199	0.0408
H(C16)	0.1928	0.1423	0.2389
H(C17)	-0.0025	0.2172	0.1209
H(C18)	0.1248	0.2466	-0.1301
H(C19)	0.3390	0.1790	-0.1968

Results and discussion

The molecular structures of (I) and (II) are shown in Figs. 1 and 2. The bond lengths and angles for the U inner coordination sphere of both complexes are summarized in Table 4; for σ -bonded groups and cyclopentadienyl rings see Table 5. The molecule of complex (I) lies on a crystallographic mirror plane passing through the U atom, a C atom, C(12), of a cyclopentadienyl ring and the CH₂-C and C-CH₃ bonds of the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31886 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

p-methylbenzyl group; on the other hand the molecule of complex (II) possesses a pseudo mirror plane. In spite of this difference, the two complexes display a very similar geometry, with the σ -bonded group and the three η^5 -cyclopentadienyl rings arranged tetrahedrally around the metal atom. However, some distortion from the regular tetrahedral coordination occurs, as is illustrated by the angles about the U atom to the σ -bonded C atom and to the centres of the three cyclopentadienyl rings (designated 1, 2 and 3 in Tables 4 and 5). The values of C(1)–U–centre-of-ring angles range from 99.4 to 99.8° in (I) and from 98.2 to 102.3° in (II), while the centre-of-ring–U–centre-of-ring angles range from 115.6 to 120.6° in (I) and from 115.8 to 118.1° in (II). These values are in good agreement with the corresponding mean values of 100 and 117° respectively, reported for $U(C_5H_5)_3(C_2C_6H_5)$ (Atwood, Hains, Tsutsui & Gebala, 1973), $U(C_5H_5)_3[CH_3C(CH_2)_2]$ (Raymond, 1975) and $U(C_5H_4CH_2C_6H_5)_3Cl$ (Leong, Hodgson & Raymond, 1973).

The C atoms of each cyclopentadienyl ring are within 0.04 Å of the best least-squares plane in both structures. The average C–C distance in the five-membered rings is 1.35 (1) Å in both complexes, slightly lower than the corresponding values of 1.374 (2) and 1.386 (5) Å reported for $U(C_5H_4CH_2C_6H_5)_3Cl$ (Leong, Hodgson & Raymond, 1973) and $U(C_5H_5)_4$ (Burns, 1974) respectively.

The average U–cyclopentadienylic C bond distance is 2.722 (4) in (I) and 2.736 (8) Å in (II); in Table 6

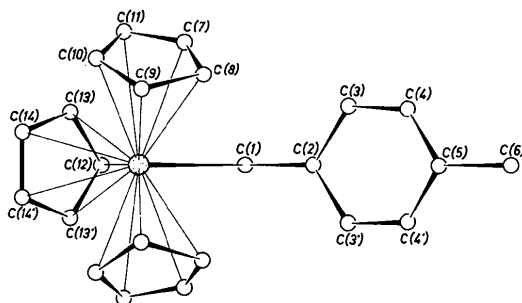


Fig. 1. A perspective view of the molecule of $U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$.

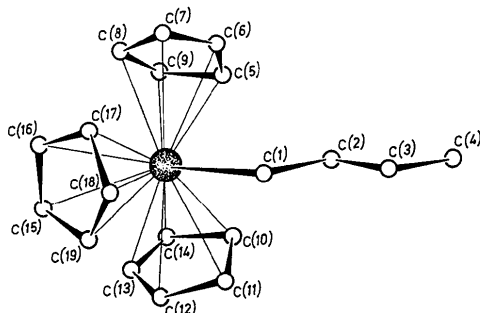


Fig. 2. A perspective view of the molecule of $U(C_5H_5)_3(n-C_4H_9)$.

Table 4. Inner-coordination-sphere bond lengths (Å) and angles (°)

	$U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$		$U(C_5H_5)_3(n-C_4H_9)$	
σ -Bond	U–C(1)	2.541 (15)	U–C(1)	2.426 (23)
Ring 1	U–C(7)	2.713 (18)	U–C(5)	2.733 (26)
	U–C(8)	2.684 (13)	U–C(6)	2.709 (26)
	U–C(9)	2.674 (19)	U–C(7)	2.733 (31)
	U–C(10)	2.725 (17)	U–C(8)	2.718 (24)
	U–C(11)	2.726 (14)	U–C(9)	2.751 (26)
	Mean U–C	2.705 (7) ^(a)	Mean U–C	2.728 (12)
	U–1 ^(b)	2.455	U–1	2.470
Ring 2 ^(c)			U–C(10)	2.759 (32)
			U–C(11)	2.648 (40)
			U–C(12)	2.701 (42)
			U–C(13)	2.763 (37)
			U–C(14)	2.768 (28)
			Mean U–C	2.738 (15)
			U–2	2.474
Ring 3	U–C(12)	2.763 (14)	U–C(15)	2.752 (27)
	U–C(13)	2.731 (12)	U–C(16)	2.823 (29)
	U–C(14)	2.744 (11)	U–C(17)	2.709 (35)
	Mean U–C	2.742 (5)	U–C(18)	2.694 (34)
			U–C(19)	2.714 (41)
			Mean U–C	2.747 (14)
	U–3	2.477	U–3	2.494
	C(1)–U–1	99.8	C(1)–U–1	98.2
			C(1)–U–2	102.3
	C(1)–U–3	99.4	C(1)–U–3	100.7
	1–U–2	120.6	1–U–2	118.1
	1–U–3	115.6	1–U–3	116.5
			2–U–3	115.8

(a) The mean values and the related standard deviations were calculated with the formulae reported in *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1965). (b) Centre of ring 1 designated as 1, etc. (c) The U–C values for ring 2 in $U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$ are equivalent to those of ring 1; the two rings are related by a crystallographic mirror plane.

these values are compared with the corresponding distances found in other complexes of general formula $U(C_5H_5)_3X$. Leong *et al.* (1973) have proposed a linear relationship between the bond length and the charge on the ligand; this predicts U^{IV}–C distances of 2.81, 2.73 and 2.65 Å for π -carbocyclic ligands having charges of 0, –1 and –2 respectively. For the compounds listed in Table 6 the mean U–C π -bond distance is not constant, as would be expected on the basis of the above relationship, but it clearly depends on the size of the atom or group of the X ligand directly bonded to the metal. This evidence suggests that steric (in addition to electronic) factors are effective in determining the metal-to-ring bond distance; a similar argument was reported by Burns (1974).

The σ -bonded nature of the *p*-methylbenzyl group in (I) and of the *n*-butyl group in (II) is clearly indicated by the two structures. All the C atoms of the *p*-methylbenzyl group lie within 0.02 Å of their mean plane. The conformation of the butyl ligand is *trans*, the internal rotation angles about the C(1)–C(2) and C(2)–C(3) bonds being 172.7 and 178.3° respectively.

The U-C σ -bond distance is 2.541 (15) in (I) and 2.426 (23) Å in (II); the intermediate value of 2.48 (3) Å has been found for the same bond in $U(C_5H_5)_3[CH_3C(CH_2)_2]$ (Raymond, 1975). In this class of complexes the U-C σ -bond possesses considerable

ionic character, as pointed out on the basis of chemical evidence by Marks, Seyam & Kolb (1973); this suggests that the shortening of the U-C distance in going from the *p*-methylbenzyl to the *n*-butyl derivative can be related to a decreasing ionic character of the bond. In fact, the amount of negative charge on the methylene group bonded to the metal should be larger in the case of the *p*-methylbenzyl derivative. The short distance of 2.33 (2) Å reported for $U(C_5H_5)_3(C_2C_6H_5)$ (Atwood *et al.*, 1973), should be ascribed to the different hybridization (in this case *sp*) of the C atom bonded to the metal.

The values of U-C(1)-C(2), 128.6 (9) and 128.5 (16)° in (I) and (II) respectively, are in agreement with the value of 127 (4)° found for the same angle in $U(C_5H_5)_3[CH_3C(CH_2)_2]$ (Raymond, 1975); these values are exceptionally large with respect to the usual *sp*³ hybridization of the methylene group. It is probable that intramolecular interactions play some role in determining the opening of this bond angle; however, the C-C contacts between the β -C [as well as the *ortho* carbons of the phenyl group in (I)] of the σ -bonded group and the cyclopentadienyl rings range from 3.5 to 3.7 Å in both complexes. It can be argued that these contacts are not sufficiently strained to justify a distortion of about 20° from the ideal tetrahedral value. In addition, the opening of this bond angle in (I) is in contrast to the reduction of the metal C-C angles to 85° observed in tetrabenzyls of Zr, Hf and Ti, for which a

Table 5. Bond lengths (Å) and angles (°) for the cyclopentadienyl and σ -bonded groups

	$U(C_5H_5)_3(p-CH_3-C_6H_4-CH_2)$		$U(C_5H_5)_3(n-C_4H_9)$		
σ -bonded group	C(1)-C(2)	1.448(22)	C(1)-C(2)	1.45(4)	
	C(2)-C(3)	1.417(15)	C(2)-C(3)	1.48(4)	
	C(3)-C(4)	1.364(17)	C(3)-C(4)	1.50(4)	
	C(4)-C(5)	1.387(15)			
	C(5)-C(6)	1.544(24)			
	U-C(1)-C(2)	128.6(9)	U-C(1)-C(2)	128.5(16)	
	C(1)-C(2)-C(3)	121.7(6)	C(1)-C(2)-C(3)	123.3(13)	
	C(2)-C(3)-C(4)	120.6(6)	C(2)-C(3)-C(4)	116.3(12)	
	C(3)-C(4)-C(5)	123.0(6)			
	C(4)-C(5)-C(6)	121.9(6)			
	C(3)-C(2)-C(1')	116.4(6)			
	C(4)-C(5)-C(4')	116.2(6)			
Ring 1	C(7)-C(8)	1.282(27)	C(5)-C(6)	1.41(4)	
	C(8)-C(9)	1.403(28)	C(6)-C(7)	1.23(4)	
	C(9)-C(10)	1.377(24)	C(7)-C(8)	1.47(4)	
	C(10)-C(11)	1.356(24)	C(8)-C(9)	1.34(4)	
	C(7)-C(11)	1.257(27)	C(5)-C(9)	1.37(4)	
	C(8)-C(7)-C(11)	119.5(8)	C(6)-C(5)-C(9)	99.1(11)	
	C(7)-C(8)-C(9)	103.5(7)	C(5)-C(6)-C(7)	117.7(16)	
	C(8)-C(9)-C(10)	103.8(7)	C(6)-C(7)-C(8)	104.9(10)	
	C(9)-C(10)-C(11)	110.7(7)	C(7)-C(8)-C(9)	104.2(12)	
	C(7)-C(11)-C(10)	102.0(7)	C(5)-C(9)-C(8)	113.8(11)	
	Ring 2 ^a			C(10)-C(11)	1.44(5)
				C(11)-C(12)	1.40(6)
			C(12)-C(13)	1.28(5)	
			C(13)-C(14)	1.22(5)	
			C(10)-C(14)	1.43(4)	
			C(11)-C(10)-C(14)	103.1(13)	
			C(10)-C(11)-C(12)	104.8(16)	
			C(11)-C(12)-C(13)	107.3(18)	
			C(12)-C(13)-C(14)	116.1(17)	
			C(10)-C(14)-C(13)	108.4(18)	
Ring 3		C(12)-C(13)	1.373(22)	C(15)-C(16)	1.28(4)
		C(13)-C(14)	1.406(27)	C(16)-C(17)	1.36(5)
	C(14)-C(14')	1.347(25)	C(17)-C(18)	1.33(5)	
			C(18)-C(19)	1.30(5)	
			C(15)-C(19)	1.38(5)	
	C(12)-C(13)-C(14)	114.6(6)	C(16)-C(15)-C(19)	112.3(16)	
	C(13)-C(14)-C(14')	105.5(7)	C(15)-C(16)-C(17)	107.6(13)	
	C(13)-C(12)-C(13')	99.7(7)	C(16)-C(17)-C(18)	103.1(15)	
			C(17)-C(18)-C(19)	115.6(18)	
			C(15)-C(19)-C(18)	100.4(16)	

^aThe geometrical parameters of ring 2 in $U(C_5H_5)_3(p-CH_3-C_6H_4-CH_2)$ are equivalent to that of ring 1, the two rings being related by a crystallographic mirror plane.

Table 6. Average U-C bond lengths for π -bonded cyclopentadienyl groups in $U(C_5H_5)_3X$

X (σ -bonded)	U-C (Å)	Reference
$C_6H_5-C\equiv C-$	2.68	Atwood, Hains, Tsutsui & Gebala (1973)
$p-CH_3-C_6H_4-CH_2-$	2.722 (4)	Present work
$CH_3-CH_2-CH_2-CH_2-$	2.736 (8)	Present work
CH_3-C-CH_2-	2.74 (1)	Raymond (1975)
CH_2-Cl-	2.74	Wong, Yen & Lee (1965)
X (π -bonded)		
C_5H_5	2.807 (11)	Burns (1974)

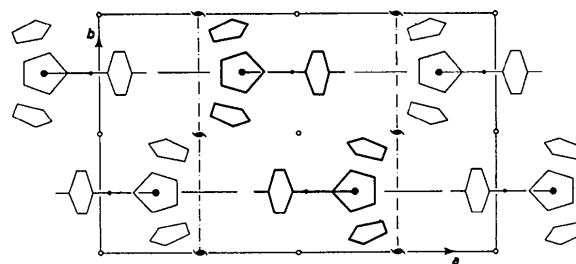


Fig. 3. The crystal structure of $U(C_5H_5)_3(p-CH_3C_6H_4CH_2)$; projection along the *c* axis.

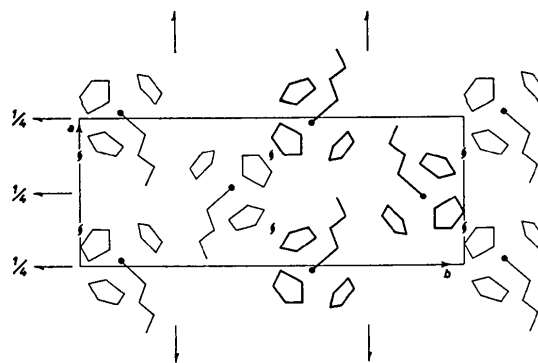


Fig. 4. The crystal structure of $U(C_5H_5)_3(n-C_4H_9)$; projection along the *c* axis.

weak attractive interaction between the metal and the aromatic ring has been postulated (Bassi, Allegra, Scordamaglia & Chioccola, 1971; Davies, Jarvis & Kilbourn, 1971). Because of the close similarity of the U-C-C bond angles in (I), (II) and $U(C_5H_5)_3[CH_3C(CH_2)_2]$, an interaction (in this case repulsive) of this type must be excluded.

This uncommon type of metal-C σ -bond is also indicated by the unusual geometry of the butyl ligand in (II). In fact, as may be seen from Table 5, the values of the C-C-C bond angles are very large and decrease from 123.3 (13) to 116.3 (12)°, going from $C_\beta-C_\gamma$, while the C-C distances are all shorter than the normal single bond. There is also an increase of the C-C bond length from 1.45 (4) (C_x-C_β) to 1.48 (4) ($C_\beta-C_\gamma$) and to 1.50 (4) Å ($C_\gamma-C_\delta$); unfortunately, the differences between these last values are within the standard deviations, and therefore this effect cannot be settled. It is worth while to mention that a similar effect occurs in the *p*-methylbenzyl group in (I): in fact CH_2-C is shortened to 1.448 (22) while C- CH_3 has the usual value of 1.544 (24) Å (in this case the difference between the two bond distances is significant as it is several times the standard deviations). This effect could be caused by an extra charge, whose amount decreases towards the external part of the ligand, received from the metal; this effect, which seems to be supported by some 1H NMR evidence (Brunelli, 1975), could be present, to a different extent, in both complexes. The fact that in the *p*-methylbenzyl derivative no relevant steric modifications occur and also that the CH_2-C distance is shortened are to be ascribed to the planarity of the ligand.

The crystal packings of (I) and (II) are shown in Figs. 3 and 4. No critical intermolecular interaction is observed since all the $C \cdots C$ contacts are greater than 3.6 Å.

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