

Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule, with thermal ellipsoids at the 50% probability level.

(Table 2), and the average U—Cp (ring-centroid) distance is 2.51 (3) Å. These distances are similar to those found in $(C_5H_7)_3U$ (Meunier-Piret, Declercq, Germain & Van Meerssche, 1980). The cyclopentadienyl rings are planar to within 0.023 Å and the silicon atom of the Me_3Si group is out of the cyclopentadienyl ring plane and pointed away from the U atom by an average distance of 0.21 Å. The coordination geometry of the molecule may be described as trigonal planar.

Comparison of the geometrical parameters between the trigonal planar $(Me_3SiC_5H_4)_3U$ and its pseudotetrahedral complex $(Me_3SiC_5H_4)_3U(CNC_2H_5)$ shows that the stereochemistry of the base-free compound is only weakly perturbed upon adduct formation. The average U—C distances are identical, 2.78 (4) and 2.81 (3) Å, respectively, as are the U—C (ring-centroid) distances of 2.51 and 2.53 Å, respectively, given the uncertainty in these values. Further, the average (ring-centroid)—U—(ring-centroid) angle is nearly un-

perturbed as it contracts from 120° in the base-free compound to 119° in the adduct. It is surprising that the stereochemistry of $(Me_3SiC_5H_4)_3U$ changes so slightly upon coordination with the sterically small ethyl isocyanide. The feeble geometrical change upon coordination with the isocyanide presumably means that the reorganization energy is also very small, which rationalizes why carbon monoxide reversibly binds to $(Me_3SiC_5H_4)_3U$ (Brennan, Andersen & Robbins, 1986).

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Dimeric Bis(di-tert-butylcyclopentadienyl)uranium Chloride

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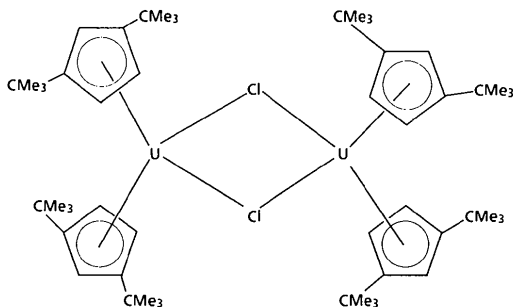
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Abstract. $[(\{(CH_3)_3C\}_2C_5H_3)_2U]_2Cl_2$, $M_r = 1256.22$, orthorhombic, $Pccn$, $a = 13.040$ (3), $b = 17.086$ (3), $c = 24.587$ (3) Å, $V = 5478$ Å³, $Z = 4$, $D_x = 1.523$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 57.24$ cm⁻¹, $F(000) = 2456$, $T = 296$ K, $R = 0.027$ [1293 data, $F^2 > 2\sigma(F^2)$]. Two $[(Me_3C)_2C_5H_3]UCl$ groups form a double chlorine-bridged dimer in which the U atom is bonded to two cyclopentadienyl rings and

to two Cl atoms with U—Cp and U—Cl distances of 2.516 and 2.856 (4) Å, respectively.

Introduction. The title compound was prepared as part of a systematic synthetic and X-ray crystallographic study aimed at elucidating the solid state stereochemistry and geometrical alterations in trivalent uranium metallocenes as a function of coordination

environment. It has been shown that the tris-cyclopentadienyl compounds of the type $(RC_5H_4)_3(L)$, where R is H or CH_3 and L is a Lewis base such as an ether, amine, thioether or phosphine, can be isolated (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983; Zalkin & Brennan, 1985, 1987; Brennan & Zalkin, 1985). When R is a sterically large group, such as Me_3Si , the base-free compound $(Me_3SiC_5H_4)_3U$ is isolated (Brennan, Andersen & Zalkin, 1986). Increasing the number of bulky substituents on the cyclopentadienyl ring by one gives the dimeric molecule $[1,3-(Me_3Si)_2C_5H_3]_4U_2(\mu-Cl)_2$ (Blake, Lappert, Taylor, Atwood, Hunter & Zhang, 1986). The title compound, $[1,3-(Me_3C)_2C_5H_3]_4U_2(\mu-Cl)_2$, is a related member of this series. The latter two compounds are an excellent pair of compounds in which the issue of intramolecular steric effects in two molecules of identical empirical formulae that differ only in the replacement of the Si atoms by C atoms may be addressed. A structural representation of the complex is shown below.



Experimental. The title compound was prepared from $K[1,3-(Me_3C)_2C_5H_3]$ and UCl_3 in tetrahydrofuran followed by crystallization from hexane as bright green crystals. An air-sensitive crystal, $0.1 \times 0.1 \times 0.25$ mm, was sealed inside a quartz capillary in an argon-filled dry box. X-ray diffraction intensities (θ - 2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer equipped with a graphite monochromator. Cell dimensions from 20 reflections, $22 < 2\theta < 34^\circ$; 2θ scan width ($1.5 + 0.693 \tan \theta$), 2θ scan speed $2-8^\circ \text{ min}^{-1}$; analytical absorption correction, range $1.72-1.90$; max. $(\sin \theta)/\lambda = 0.60 \text{ \AA}^{-1}$, h 0 to 15, k -20 to 19, l 0 to 14; three standard reflections, 1.4%, 1.0%, 4.3% variation in standards' intensities from average, intensities adjusted isotropically; 5477 data, 2629 unique (with 1293 $F^2 > 2\sigma$), $R_{\text{int}} = 0.072$; structure solved by Patterson and Fourier methods; refined on F , 254 parameters; 42 H atoms in calculated positions and fixed isotropic thermal parameters; anisotropic thermal parameters for non-hydrogen atoms; $R = 0.12$ for all the data, $R = 0.027$ for $F^2 > 2\sigma$ data, $wR = 0.021$, $S = 1.01$; $w = 4F^2[\sigma^2(F^2) + (0.02F^2)^2]^{-1}$; max. $(\text{shift}/\sigma) = 0.14$; no extinction correction indicated; max. and min. of ΔF synthesis 3.3

Table 1. Atomic parameters

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
U(1)	$\frac{1}{2}$	$\frac{1}{2}$	0.29597 (3)	3.38 (2)
U(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.11133 (2)	3.53 (2)
Cl	0.34838 (28)	0.18173 (22)	0.20369 (18)	4.2 (1)
C(1)	0.4315 (12)	0.3388 (10)	0.3085 (6)	4.3 (6)
C(2)	0.3501 (14)	0.3894 (9)	0.3226 (7)	4.4 (6)
C(3)	0.3094 (10)	0.3609 (10)	0.3723 (6)	3.1 (5)
C(4)	0.3638 (12)	0.2915 (9)	0.3847 (8)	4.1 (5)
C(5)	0.4378 (12)	0.2780 (8)	0.3467 (6)	3.9 (5)
C(6)	0.3645 (16)	0.3900 (11)	0.1003 (7)	5.2 (7)
C(7)	0.2806 (11)	0.3994 (11)	0.0632 (6)	3.9 (6)
C(8)	0.2990 (14)	0.3402 (10)	0.0242 (8)	5.9 (6)
C(9)	0.3883 (14)	0.2977 (9)	0.0336 (7)	4.8 (6)
C(10)	0.4306 (15)	0.3298 (12)	0.0829 (8)	5.2 (7)
C(11)	0.3325 (14)	0.4719 (10)	0.2998 (11)	3.7 (5)
C(12)	0.3705 (15)	0.4785 (9)	0.2431 (8)	8.2 (7)
C(13)	0.3826 (16)	0.5314 (10)	0.3345 (8)	8.8 (8)
C(14)	0.2148 (12)	0.4904 (12)	0.2980 (12)	5.9 (8)
C(15)	0.5267 (12)	0.2195 (9)	0.3504 (7)	4.8 (6)
C(16)	0.5965 (11)	0.2431 (19)	0.3961 (7)	8.9 (7)
C(17)	0.5917 (13)	0.2171 (11)	0.2988 (8)	9.4 (9)
C(18)	0.4880 (13)	0.1375 (11)	0.3635 (10)	10.2 (9)
C(19)	0.2033 (15)	0.4635 (11)	0.0624 (8)	6.4 (8)
C(20)	0.231 (3)	0.5217 (10)	0.0216 (8)	12.5 (10)
C(21)	0.1933 (15)	0.5066 (11)	0.1174 (10)	9.5 (9)
C(22)	0.0988 (15)	0.4313 (11)	0.0488 (10)	10.7 (9)
C(23)	0.5381 (15)	0.3129 (15)	0.1019 (10)	5.3 (8)
C(24)	0.5530 (11)	0.3334 (11)	0.1613 (7)	7.0 (6)
C(25)	0.6111 (14)	0.3700 (12)	0.0693 (7)	8.7 (7)
C(26)	0.5748 (15)	0.2329 (22)	0.0929 (11)	11.4 (19)

Table 2. Selected distances (\AA) and angles ($^\circ$)

$\langle U(1)-C \rangle$	2.78 (4)	$U(1)-Cl$	2.856 (4)
$\langle U(2)-C \rangle$	2.79 (5)	$U(2)-Cl'$	2.857 (4)
$U(1)-Cp(1)$	2.516	$U(1)-U(2)$	4.540 (1)
$U(2)-Cp(2)$	2.516	$Cl-Cl$	3.468 (7)
$Cp(1)-U(1)-Cp(1')$	120.2	$Cp(2)-U(2)-Cl'$	110.5
$Cp(2)-U(2)-Cp(2')$	120.9	$Cl-U(1)-Cl'$	74.77 (17)
$Cp(1)-U(1)-Cl$	108.9	$Cl-U(2)-Cl'$	74.73 (15)
$Cp(1)-U(1)-Cl'$	117.9	$U(1)-Cl-U(2)$	105.25 (11)
$Cp(2)-U(2)-Cl$	115.8		

$Cp(1)$ and $Cp(2)$ are the centroids of cyclopentadienyl ring atoms $C(1)-C(5)$ and $C(6)-C(10)$ respectively. $Cp(1')$, $Cp(2')$ and Cl' represent the equivalent groups or atoms at $\frac{1}{2}-x$, $\frac{1}{2}-y$, z .

and $-3.7 e \text{ \AA}^{-3}$; atomic f for neutral U, Cl and C, and spherical bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965). Atomic parameters are listed in Table 1.* A list of selected distances and angles is given in Table 2. Fig. 1 shows the molecule and its numbering scheme.

Discussion. The compound is a dimer in which the U atom is bonded to two cyclopentadienyl rings in a penta-

* Lists of anisotropic thermal parameters, calculated hydrogen positions, least-squares planes, distances and angles and additional *ORTEP* drawings have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51197 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hapto fashion and to two chlorides which bridge the two U atoms. The cyclopentadienyl rings are rigorously planar but the tertiary C atoms of the *tert*-butyl groups are out of the cyclopentadienyl ring plane and directed away from the U atom by an average of 0.27 (4) Å. The rings of the bent sandwich molecule are in a staggered configuration with respect to each other about both the U(1) and U(2) atoms. The averaged U—C distance of 2.79 (4) Å and the U—Cp(centroid) distance of 2.51 Å are not significantly different from these values in other trivalent uranium metallocenes. The averaged U—Cl distance of 2.856 (1) Å is in the range found in other trivalent uranium compounds with bridging chloride ligands which range from 2.78 (1) Å in [(Me₆C₆)₃]U₃(μ-Cl)₃(μ₃-Cl)₂(μ-Cl₂AlCl₂)₃(AlCl₄) (Cotton, Schwotzer & Simpson, 1986), 2.810 (1) Å in [1,3-(Me₃Si)₂C₅H₃]₄U₂(μ-Cl)₂ (Blake, Lappert, Taylor, Atwood, Hunter & Zhang, 1986), and 2.90 (1) Å in [Me₃C₅]₆U(μ-Cl)₃ (Fagan, Manriquez, Marks, Day, Vollmer & Day, 1982).

A comparison between the geometrical parameters in [1,3-(Me₃Si)₂C₅H₃]₄U₂(μ-Cl)₂ and [1,3-(Me₃C)₂C₅H₃]₄U₂(μ-Cl)₂ is shown in Table 3. The U—Cl distance in the (Me₃C)₂C₅H₃ compound is 0.046 Å longer and the U...U distance is 0.183 Å longer than the equivalent distances in the (Me₃-Si)₂C₅H₃ compound. As a consequence the Cl—U—Cl in the (Me₃C)₂C₅H₃ compound is closed by 4°, the Cp—U—Cp angle is closed by 11° and the U—Cl—U

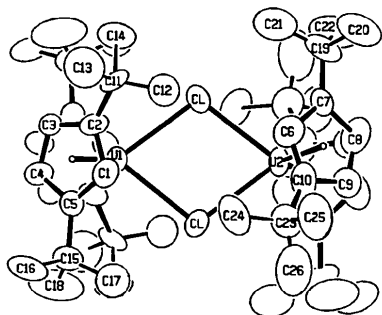


Fig. 1. ORTEP drawing (Johnson, 1965) with thermal ellipsoids at 50% probability level.

Table 3. Bond lengths and angles comparison

	[(Me ₃ Si) ₂ C ₅ H ₃] ₄ U ₂ (μ-Cl) ₂	[(Me ₃ C) ₂ C ₅ H ₃] ₄ U ₂ (μ-Cl) ₂
U—C(ave) (Å)	2.78 (2)	2.78 (4)
U—Cp(ave) (Å)	2.50	2.52
U—Cl(ave) (Å)	2.710 (4)	2.856 (1)
U...U (Å)	4.357 (1)	4.540 (1)
Cl—U—Cl (°)	78.5 (1)	74.7 (2)
Cl—U—Cp(ave) (°)	107	113
Cp—U—Cp(ave) (°)	131	120
U—Cl—U (°)	101.5	105.3 (1)

angle is opened by 4° relative to the equivalent angles in the (Me₃Si)₂C₅H₃ compound. The geometry changes are small though they may be rationalized by the well established fact that Me₃C groups are sterically larger than Me₃Si groups. Thus the (Me₃C)₂C₅H₃ groups cannot approach each other as close as the (Me₃-Si)₂C₅H₃ groups can, and this accounts for the geometry changes listed in Table 3.

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