A comparison of the structural ring parameters from $Re_2(\mu\text{-}P)_2$ to $Re_2(\mu\text{-}P)(\mu\text{-}Sb)$ shows that the angle subtended at the Re atoms is only reduced by about 2·3 (1)°, whereas that at the P atoms is distinctly enlarged by 7·8 (1)°. This means that the previously mentioned isovalent exchange realizes for the remaining μ-P atom a better approximation to an idealized sp^3-hybridization state in such rings of the type $M_2(\mu\text{-}P)_2$ (Mason & Mingos, 1973). In addition, the last-named ring type has, in the absence of steric expanded groups bound to the ring atoms, the following ring bond angles (av.): P—*M*—P 75–78° and *M*—P—*M* 102–105°. Each range of these bond angles has been found not only for different transition-metal atoms *M* but also for various ligands attached at the ring atoms (Deppisch *et al.*, 1984). Compared to the μ-P bond-angle alteration in the title substances, the examined exchange of isovalent bridging atoms has a more distinct effect.

The average Re—P bond lengths of both the rhenium compounds do not differ significantly. The covalent single-bond length of an Re—Sb bond has been measured for the first time; its value of 2·671 (1) Å in the terminal coordinated $SbPh_3$ group is shorter than that of 2·740 (1) Å (av.) in the bridging diphenylantimonido group.

Intermolecular distances in the title compounds do not indicate interactions greater than van der Waals forces.

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Tris(trimethylsilylcyclopentadienyl)uranium(III)

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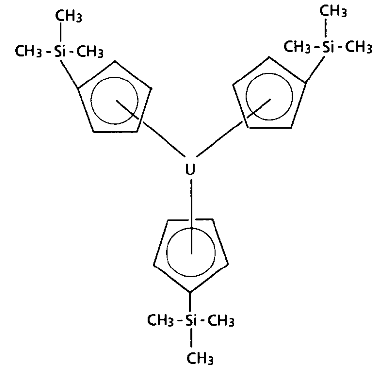
Abstract. [$\{(CH_3)_3SiC_5H_4\}_3U$], $M_r = 649·87$, orthorhombic, *Pbca*, $a = 22·630\,(8)$, $b = 29·177\,(10)$, $c = 8·428\,(3)$ Å, $V = 5564·8$ Å^3, $Z = 8$, $D_x = 1·551$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 56·64$ cm^{-1}, $F(000) = 2536$, $T = 296$ K, $R = 0·041$ [2251 data, $F^2 > 2\sigma(F^2)$]. The U 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 Å, and the average U—C distance is 2·78 (4) Å.

Introduction. The title compound was prepared as part of a systematic synthetic and X-ray crystallographic investigation of the role of steric effects on the stereochemistry of trivalent metallocenes. Trivalent uranium metallocenes form compounds of the type $(RC_5H_4)_3U(L)$ where *R* is either H or CH_3 and *L* is a Lewis base such as tetrahydrofuran (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983), tetrahydrothiophene (Zalkin & Brennan, 1985), 4-dimethylaminopyridine (Zalkin & Brennan, 1987), trimethylphosphine (Brennan & Zalkin, 1985), or 1,2-bis(dimethylphosphino)ethane (Zalkin, Brennan & Andersen, 1987). All of these molecules may be described as four-coordinate complexes of trivalent uranium (defining the midpoint of the cyclopentadienyl ring centroid as occupying one coordination position) with a distorted tetrahedral stereochemistry. Increasing the size of the substituent on the cyclopentadienyl ring to Me_3Si gives monomeric base-free $(Me_3SiC_5H_4)_3U$ (Brennan, Andersen & Zalkin, 1986), the title compound, the structure of which was determined in order to compare its geometrical parameters with those of the 1:1 coordination complex $(Me_3SiC_5H_4)_3U(CNC_2H_5)$ (Brennan, Andersen & Robbins, 1986). A structural formula of the molecule is shown below.



Experimental. The title compound was prepared as previously described (Brennan, Andersen & Zalkin, 1986) and crystallized from hexane (193 K). A green air-sensitive crystal, 0·21 × 0·30 × 0·48 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 29 reflections, $24 < 2\theta < 33°$; analytical absorption correction, range 2·99 to 4·82; max. $(\sin\theta)/\lambda = 0{\cdot}60$ Å^{-1}, h 0 to 26, k 0 to 34, l −10 to 10; three standard reflections, 30% isotropic variation in standards' intensities from average, intensities adjusted accordingly; 7595 data, 4904 unique [2251 for which $F^2 > 2\sigma(F^2)$], $R_{\rm int} = 0{\cdot}054$; structure solved by Patterson and Fourier methods; refined on F, 253 parameters; 12 non-methyl H atoms in calculated positions and fixed isotropic thermal parameters, methyl H atoms not included, anisotropic thermal parameters for all non-hydrogen atoms; $R = 0{\cdot}15$ for all the data, $R = 0{\cdot}041$ for $F^2 > 2\sigma(F^2)$ data, $wR = 0{\cdot}041$, $S = 1{\cdot}22$; $w = 4F^2[\sigma^2(F^2) + (0{\cdot}04F^2)^2]^{-1}$; max. $(\text{shift}/\sigma) = 0{\cdot}03$; no extinction correction indicated; max., min. of ΔF synthesis 1·8 and −2·3 e Å^{-3}; atomic f for neutral U, Si, 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,* and distances and angles are listed in Table 2. Fig. 1 shows the molecule and the numbering scheme.

Table 1. *Atomic parameters*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
U	0·22514 (2)	0·12380 (2)	0·08037 (6)	3·47 (1)
Si(1)	0·10228 (21)	0·02486 (15)	0·2233 (7)	5·9 (2)
Si(2)	0·37799 (21)	0·17835 (16)	0·2461 (8)	6·4 (2)
Si(3)	0·08792 (20)	0·14995 (15)	−0·2207 (7)	5·9 (2)
C(1)	0·1792 (7)	0·0451 (4)	0·2281 (20)	4·1 (5)
C(2)	0·2263 (10)	0·0286 (5)	0·1363 (19)	5·1 (5)
C(3)	0·2812 (10)	0·0449 (6)	0·1966 (27)	6·1 (7)
C(4)	0·2641 (12)	0·0707 (7)	0·343 (3)	7·7 (8)
C(5)	0·2042 (10)	0·0718 (6)	0·3510 (22)	6·2 (6)
C(6)	0·2976 (7)	0·1887 (5)	0·2182 (21)	4·3 (5)
C(7)	0·2505 (9)	0·1824 (7)	0·3197 (25)	6·0 (8)
C(8)	0·1979 (8)	0·2001 (5)	0·2570 (29)	5·9 (6)
C(9)	0·2125 (9)	0·2171 (5)	0·1063 (23)	5·5 (6)
C(10)	0·2725 (10)	0·2113 (4)	0·0833 (21)	5·2 (5)
C(11)	0·1650 (6)	0·1312 (5)	−0·2127 (15)	4·3 (4)
C(12)	0·1860 (9)	0·0845 (5)	−0·2028 (19)	5·9 (6)
C(13)	0·2479 (9)	0·0854 (7)	−0·2063 (23)	6·6 (7)
C(14)	0·2694 (7)	0·1310 (6)	−0·2292 (18)	5·4 (5)
C(15)	0·2162 (7)	0·1582 (5)	−0·2296 (18)	4·5 (5)
C(16)	0·0477 (8)	0·0747 (6)	0·229 (3)	10·1 (8)
C(17)	0·0902 (9)	−0·0116 (8)	0·408 (3)	10·6 (9)
C(18)	0·0899 (8)	−0·0123 (6)	0·0435 (28)	8·2 (8)
C(19)	0·4193 (9)	0·2355 (6)	0·237 (3)	10·0 (8)
C(20)	0·4058 (8)	0·1407 (7)	0·078 (3)	9·7 (8)
C(21)	0·3937 (8)	0·1506 (6)	0·4463 (23)	8·0 (7)
C(22)	0·0349 (7)	0·0989 (5)	−0·242 (3)	8·0 (6)
C(23)	0·0798 (9)	0·1874 (7)	−0·401 (3)	12·2 (10)
C(24)	0·0642 (9)	0·1863 (7)	−0·044 (3)	10·5 (9)

Table 2. *Selected distances* (Å) *and angles* (°)

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)	2·54
U–C(14)	2·802 (16)	U–Cp(2)	2·48
U–C(15)	2·806 (14)	U–Cp(3)	2·51

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)		

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.

Discussion. The title compound is a monomolecular complex of uranium bonded to three trimethylsilylcyclopentadienyl ligands in a pentahapto fashion. The U atom lies in the plane of the three cyclopentadienyl centroids with Cp—U—Cp angles all close to 120° (Table 2); the average U—C distance is 2·78 (4) Å

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51199 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

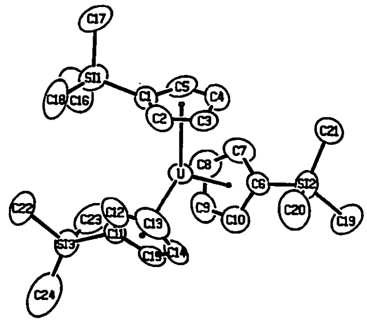

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the title molecule, with thermal ellipsoids at the 50% probability level.

(Table 2), and the average U—Cp(ring-centroid) distance is 2·51 (3) Å. These distances are similar to those found in $(C_9H_7)_3U$ (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 pseudo-tetrahedral 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 unperturbed 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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Abstract. $[(\{(CH_3)_3C\}_2C_5H_3)_2U]_2Cl_2$, $M_r = 1256{\cdot}22$, orthorhombic, *Pccn*, $a = 13{\cdot}040$ (3), $b = 17{\cdot}086$ (3), $c = 24{\cdot}587$ (3) Å, $V = 5478$ Å^3, $Z = 4$, $D_x = 1{\cdot}523$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 57{\cdot}24$ cm^{-1}, $F(000) = 2456$, $T = 296$ K, $R = 0{\cdot}027$ [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

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