platine(II) [1,79 (1) Å] (Delafontaine, Khodadad, Toffoli & Rodier, 1985). Les angles Pt—S—C(1) et Pt—S—C(2) diffèrent relativement peu de la valeur idéale prévue par l'hybridation sp^3. Par contre, C(1)—S—C(2) vaut seulement 100,4 (3)°. Dans $[Ir_2Cl_6\{S(C_2H_5)_2\}_4]$ déjà cité, les valeurs extrêmes des mêmes angles sont de 99 (1) et de 105 (1)° (Williams *et al.*, 1980).

La Fig. 2 montre que la structure peut être considérée comme formée de couches de molécules dont les positions moyennes sont les plans $x = \frac{1}{2}$.

Références

ADAMS, D. M. & CHANDLER, P. J. (1967). *J. Chem. Soc. A*, pp. 1009–1013.

BRADDOCK, P. D., ROMEO, R. & TOBE, M. L. (1974). *Inorg. Chem.* **13**, 1170–1175.

DELAFONTAINE, J.-M., KHODADAD, P., TOFFOLI, P. & RODIER, N. (1985). *Acta Cryst.* C**41**, 702–703.

FRENZ, B. A. (1982). *Structure Determination Package*. B. A. Frenz & Associates, Inc., College Station, Texas, USA, et Enraf–Nonius, Delft, Pays-Bas.

GOGGIN, P. L., GOODFELLOW, R. J., HADDOCK, S. R., KNIGHT, J. R., REED, F. J. S. & TAYLOR, B. F. (1974). *J. Chem. Soc. Dalton Trans.* pp. 523–533.

GRAY, L. R., GULLIVER, D. J., LEVASON, W. & WEBSTER, M. (1982). *Acta Cryst.* B**38**, 3079–3080.

HAMBLEY, T. W. (1986). *Acta Cryst.* C**42**, 49–51.

International Tables for X-ray Crystallography (1974). Tome IV, pp. 99 et 149. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MELANSON, R. & ROCHON, F. D. (1977). *Acta Cryst.* B**33**, 3571–3573.

MELANSON, R. & ROCHON, F. D. (1978*a*). *Acta Cryst.* B**34**, 941–943.

MELANSON, R. & ROCHON, F. D. (1978*b*). *Acta Cryst.* B**34**, 1125–1127.

PRICE, J. H., WILLIAMSON, A. N., SCHRAMM, R. F. & WAYLAND, B. B. (1972). *Inorg. Chem.* **11**, 1280–1284.

SALES, D. L., STOKES, J. & WOODWARD, P. (1968). *J. Chem. Soc. A*, pp. 1852–1858.

VEER, J. L. VAN DER, HINRICHS, W. & REEDIJK, J. (1986). *Acta Cryst.* C**42**, 534–535.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 159–166.

WILLIAMS, A. F., FLACK, H. D. & VINCENT, M. G. (1980). *Acta Cryst.* B**36**, 1206–1208.

Acta Cryst. (1987). C**43**, 1706–1708

μ-[Ethylenebis(dimethylphosphine)]-bis[tris(cyclopentadienyl)uranium(IV)]

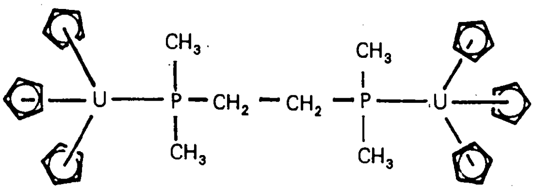
BY ALLAN ZALKIN, JOHN G. BRENNAN AND RICHARD A. ANDERSEN

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley CA 94720, USA

(*Received* 18 *November* 1986; *accepted* 10 *March* 1987)

Abstract. $[(C_5H_5)_3U\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}U(C_5H_5)_3]$, M_r = 1016·78, triclinic, $P\bar{1}$, a = 14·467 (8), b = 14·819 (6), c = 8·378 (3) Å, α = 102·72 (3), β = 90·03 (3), γ = 96·69 (3)°, V = 1739·5 Å^3, Z = 2, D_x = 1·941 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 89·3 cm^{-1}, $F(000)$ = 952, T = 296 K, R = 0·035 for 1987 unique reflections with $F^2 > 2\sigma(F^2)$ of 3241 total unique data. The P atom at each end of the ethylene(dimethylphosphine) ligand is coordinated to a trivalent U atom of a tris(cyclopentadienyl)uranium fragment; a center of inversion is located at the midpoint of the CH_2CH_2 bridge of the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ligand. Distance (Å) are: ave. U—C(Cp) 2·77 (3); ave. U—P 3·022 (2); ave. U—Cp(centroid) 2·52 (1) Å.

Introduction. The title complex was prepared during the course of studies on the coordination chemistry of tetra- and trivalent uranium complexes with bidentate amine, phosphine and arsine ligands. The crystal structures of the tetravalent complexes with bidentate ligands, $UCl_4[(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$ (Zalkin, Edwards, Zhang & Andersen, 1986), $U(OC_6H_5)_4[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ (Edwards, Andersen & Zalkin, 1981), $UCl_4[1,2\text{-}(CH_3)_2AsC_6H_4]_2$ (Edwards, Andersen & Gellert, 1987), and $U(CH_3)(CH_2C_6H_5)_3.(CH_3)_2PCH_2CH_2P(CH_3)_2$ (Edwards, Andersen & Zalkin, 1984) have been described. In all of the above cases the ligands are bidentate chelating ligands towards the U atom. In the title compound the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ligand is not acting as a bidentate chelating ligand but it is acting as a bridging monodentate ligand towards each trivalent U atom.



Experimental. The compound was prepared from $(C_5H_5)_3U.OC_4H_8$ and $(CH_3)_2PCH_2CH_2P(CH_3)_2$.

0108-2701/87/091706-03$01.50

Crystals suitable for X-ray diffraction studies were grown from a mixture of toluene and hexane (Brennan, 1985). Dark red air-sensitive crystals were sealed inside quartz capillaries under argon. Crystal 0·06 × 0·15 × 0·21 mm with ten faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 49 reflections, $20 < 2\theta < 36°$; analytical absorption correction, range 1·75–4·04; max. $(\sin\theta)/\lambda = 0{\cdot}48$ Å^{-1} (most of the intensities beyond this limit were unobservable); h −13 to 13, k −13 to 13, l −8 to 8; three standard reflections, average decay 3%, intensities adjusted accordingly; 6454 data, 3242 unique, $R_{\rm int} = 0{\cdot}05$; structure solved by Patterson and Fourier methods; refined on F, f' and f'' terms included, 355 parameters; calculated positional coordinates of the cyclopentadienyl H atoms with isotropic thermal parameters were included but not refined; anisotropic thermal parameters for non-hydrogen and non-disordered atoms; large thermal anisotropies and unsatisfactory distances in the ethylenebis(dimethylphosphine) ligand suggested disorder; difference electron density maps were used to locate alternative atomic positions for the ethylenebis(dimethylphosphine) C atoms; each of the C atoms in the ligand was placed in two positions and refined as a half atom with isotropic thermal parameters; occupancy factors not refined; distance restraints (Waser, 1963) imposed on disordered atoms, C—P 1·85 (2), C—C 1·54 (2), C—C(next neighbor) 3·03 (4) Å; $R = 0{\cdot}035$ for 1987 reflections for which $F^2 > 2\sigma(F^2)$; $R = 0{\cdot}086$ all data; $wR = 0{\cdot}040$; $S = 1{\cdot}0$; $w = 4F_o/[\sigma^2(F_o^2) + (0{\cdot}06F_o^2)^2]$; max. (shift/$\sigma$) < 0·04; no extinction correction; max. and min. of ΔF synthesis 2·4 and −1·2 e Å^{-3}; atomic f, f' and f'' for neutral U, Cl, P 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, and distances and angles are listed in Table 2.* Fig. 1 shows the molecule and numbering scheme.

Discussion. The structure consists of a $(C_5H_5)_3U$ fragment coordinated to each phosphorus atom of the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ligand. The phosphine ligand bridges the two $(C_5H_5)_3U$ fragments so that $(CH_3)_2PCH_2CH_2P(CH_3)_2$ acts as a monodentate ligand towards each U center. There are two crystallographically independent, though chemically equivalent, molecules in the unit cell across the inversion centers at $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},0)$.

Table 1. *Atomic parameters*

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

	x	y	z	$B/B_{\rm eq}$(Å^2)
Molecule 1				
U(1)	−0·03723 (5)	0·28914 (6)	0·54961 (9)	3·19
P(1)	−0·1054 (4)	0·0982 (4)	0·6049 (7)	4·67
C(1)	0·1520 (18)	0·350 (3)	0·603 (4)	7·85
C(2)	0·1105 (21)	0·3966 (17)	0·736 (4)	5·76
C(3)	0·0786 (16)	0·3304 (28)	0·8264 (27)	6·05
C(4)	0·1012 (23)	0·2433 (20)	0·741 (4)	6·29
C(5)	0·1462 (21)	0·2575 (23)	0·605 (4)	6·24
C(6)	0·0309 (25)	0·288 (4)	0·244 (3)	8·27
C(7)	0·0261 (27)	0·2003 (28)	0·248 (3)	5·95
C(8)	−0·064 (3)	0·1709 (20)	0·2382 (27)	5·55
C(9)	−0·1162 (19)	0·243 (4)	0·2391 (28)	7·40
C(10)	−0·054 (4)	0·3199 (23)	0·240 (3)	6·76
C(11)	−0·153 (3)	0·354 (3)	0·801 (4)	7·23
C(12)	−0·2067 (27)	0·302 (3)	0·698 (7)	11·69
C(13)	−0·2138 (29)	0·345 (5)	0·568 (5)	14·60
C(14)	−0·145 (4)	0·426 (3)	0·615 (5)	10·00
C(15)	−0·1178 (20)	0·4281 (24)	0·757 (6)	7·50
C(31)	−0·0226 (23)	0·0081 (24)	0·5841 (23)	4·7 (10)
C(32)	−0·2149 (20)	0·041 (3)	0·488 (5)	5·0 (12)
C(33)	−0·140 (3)	0·108 (3)	0·8241 (26)	5·9 (14)
C(31′)	−0·0531 (7)	−0·0060 (17)	0·486 (4)	3·7 (9)
C(32′)	−0·2332 (14)	0·067 (3)	0·545 (5)	6·0 (15)
C(33′)	−0·1021 (29)	0·0856 (29)	0·8223 (24)	3·8 (10)
Molecule 2				
U(2)	0·45618 (5)	0·21069 (6)	0·02519 (9)	3·34
P(2)	0·3991 (4)	0·4051 (4)	0·1139 (7)	4·87
C(16)	0·5210 (28)	0·1505 (28)	−0·286 (3)	7·48
C(17)	0·5171 (22)	0·2443 (24)	−0·2770 (27)	5·75
C(18)	0·4277 (25)	0·2602 (20)	−0·2729 (27)	4·97
C(19)	0·3734 (19)	0·1765 (23)	−0·287 (3)	5·48
C(20)	0·4306 (29)	0·1103 (22)	−0·294 (3)	6·87
C(21)	0·5700 (23)	0·260 (4)	0·300 (4)	9·10
C(22)	0·5969 (21)	0·176 (4)	0·220 (6)	9·20
C(23)	0·6414 (23)	0·1925 (27)	0·085 (5)	8·48
C(24)	0·6404 (16)	0·2826 (26)	0·086 (3)	5·60
C(25)	0·6014 (23)	0·3267 (23)	0·217 (5)	7·04
C(26)	0·295 (3)	0·2077 (23)	0·205 (8)	10·59
C(27)	0·2724 (22)	0·150 (4)	0·068 (6)	9·00
C(28)	0·3096 (27)	0·0762 (27)	0·024 (4)	7·30
C(29)	0·3649 (23)	0·0727 (27)	0·154 (6)	8·25
C(30)	0·3524 (28)	0·151 (3)	0·2671 (29)	8·25
C(34)	0·4905 (24)	0·5015 (23)	0·0905 (14)	5·6 (11)
C(35)	0·2916 (20)	0·425 (3)	0·008 (5)	4·8 (11)
C(36)	0·373 (3)	0·433 (4)	0·3377 (25)	7·4 (17)
C(34′)	0·4473 (7)	0·4971 (24)	0·004 (5)	5·7 (12)
C(35′)	0·2710 (13)	0·4003 (29)	0·061 (5)	4·6 (11)
C(36′)	0·407 (3)	0·465 (3)	0·3361 (24)	5·7 (13)

Primed atoms indicate the alternative disorder sites.

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

U(1)—P(1)	3·020 (06)	U(2)—P(2)	3·024 (06)
U(1)—C(1)	2·784 (28)	U(2)—C(16)	2·766 (25)
U(1)—C(2)	2·765 (25)	U(2)—C(17)	2·809 (20)
U(1)—C(3)	2·774 (22)	U(2)—C(18)	2·797 (23)
U(1)—C(4)	2·801 (25)	U(2)—C(19)	2·795 (26)
U(1)—C(5)	2·803 (27)	U(2)—C(20)	2·759 (27)
U(1)—C(6)	2·738 (25)	U(2)—C(21)	2·742 (30)
U(1)—C(7)	2·787 (26)	U(2)—C(22)	2·771 (27)
U(1)—C(8)	2·803 (24)	U(2)—C(23)	2·780 (27)
U(1)—C(9)	2·752 (24)	U(2)—C(24)	2·755 (24)
U(1)—C(10)	2·744 (23)	U(2)—C(25)	2·810 (30)
U(1)—C(11)	2·768 (21)	U(2)—C(26)	2·779 (28)
U(1)—C(12)	2·758 (33)	U(2)—C(27)	2·754 (28)
U(1)—C(13)	2·772 (30)	U(2)—C(28)	2·734 (26)
U(1)—C(14)	2·666 (27)	U(2)—C(29)	2·727 (25)
U(1)—C(15)	2·758 (23)	U(2)—C(30)	2·763 (22)
U(1)—Cp(1)	2·527	U(2)—Cp(4)	2·533
U(1)—Cp(2)	2·516	U(2)—Cp(5)	2·523
U(1)—Cp(3)	2·505	U(2)—Cp(6)	2·506
Cp(1)—U(1)—Cp(2)	117·31	Cp(4)—U(2)—Cp(5)	119·42
Cp(1)—U(1)—Cp(3)	117·61	Cp(4)—U(2)—Cp(6)	116·12
Cp(2)—U(1)—Cp(3)	119·77	Cp(5)—U(2)—Cp(6)	119·49

Cp(1), Cp(2), Cp(3), Cp(4), Cp(5) and Cp(6) represent the centroids of cyclopentadienyl atoms C(1)–C(5), C(6)–C(10), C(11)–C(15), C(16)–C(20), C(21)–C(25) and C(26)–C(30) respectively.

---

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions, distances and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43861 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

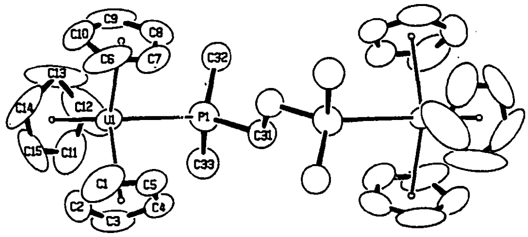


Fig. 1. *ORTEP* (Johnson, 1965) drawing of molecule 1; 50% probability ellipsoids.

The geometry of the complex is unusual since $(CH_3)_2PCH_2CH_2P(CH_3)_2$ usually acts as a bidentate ligand towards a given metal center, rather than as a bridging ligand as found in the title compound. The reason for this structural change presumably is steric, since in a hypothetical molecule, $(C_5H_5)_3U.(CH_3)_2PCH_2CH_2P(CH_3)_2$ in which the phosphine acts as a bidentate ligand, the coordination number of the U is one greater than found in the title compound. Inspection of the *ORTEP* diagram in Fig. 1 clearly shows that the molecule is economically arranged and that increasing the coordination number by one would require a substantial reorganization of the coordination sphere about U so that the intramolecular ligand–ligand repulsions are minimized. The coordination geometry about each uranium atom is similar to that found in $(CH_3C_5H_4)_3U.P(CH_3)_3$ (Brennan & Zalkin, 1985), in which the U—P distance is 2·972 (6) Å. In the title compound the averaged U—P distance is 3·022 (2) Å; the other bond lengths in these two molecules are also similar. The averaged U—C($CH_3C_5H_4$) distance in $(CH_3C_5H_4)_3U.P(CH_3)_3$ is 2·79 (4) Å and the U–(ring centroid) distance is 2·52 (1) Å, the (ring centroid)—U–(ring centroid) angle is 112 (7)° and the (ring centroid)—U—P angle is 106 (9)°. In the title complex, the averaged U—C(C_5H_5) distance is 2·77 (3) Å, the U–(ring centroid) distance is 2·52 (1) Å, the (ring centroid)—U–(ring centroid) angle is 118 (1)° and the (ring centroid)—U—P angle is 98 (1)°. Given the large uncertainty in the bond parameters and the range in individual parameters, the coordination geometries about the trivalent U atoms in the title compound and in $(CH_3C_5H_4)_3U.P(CH_3)_3$ are essentially the same.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098.

References

Brennan, J. G. (1985). PhD Thesis. Univ. of California at Berkeley, California, USA.

Brennan, J. G. & Zalkin, A. (1985). *Acta Cryst.* C**41**, 1038–1040.

Edwards, P. G., Andersen, R. A. & Gellert, R. W. (1987). In preparation.

Edwards, P. G., Andersen, R. A. & Zalkin, A. (1981). *J. Am. Chem. Soc.* **103**, 7792–7793.

Edwards, P. G., Andersen, R. A. & Zalkin, A. (1984). *Organometallics*, **3**, 293–298.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2, pp. 71–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Waser, J. (1963). *Acta Cryst.* **16**, 1091–1094.

Zalkin, A., Edwards, P. G., Zhang, D. & Andersen, R. A. (1986). *Acta Cryst.* C**42**, 1480–1482.

Acta Cryst. (1987). C**43**, 1708–1709

Structure of Tetrakis(methyldiphenylphosphine)iridium(I) Tetrafluoroborate with Cyclohexane of Solvation: a Reappraisal

By G. R. Clark,* B. W. Skelton and T. N. Waters

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

and J. E. Davies

Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 20 *October* 1986; *accepted* 27 *April* 1987)

Abstract. $[Ir\{P(C_6H_5)_2CH_3\}_4]BF_4.\frac{2}{3}C_6H_{12}$, $M_r = 1135·95$, rhombohedral, $R\bar{3}c$, $a = 22·895$ (4), $c = 51·535$ (5) Å, $U = 23394$ Å^3, $Z = 18$, $D_m = 1·49$, $D_x = 1·45$ Mg m^{-3}, $F(000) = 10\,332$. This structure has been reported [Clark, Skelton & Waters (1975). *J. Organomet. Chem.* **85**, 375–394] as monoclinic, space group *C*2/*c*. The original *C*2/*c* reflexion data (7905 reflexions) have been transformed to a rhombohedral

---

* To whom all correspondence should be addressed.

0108-2701/87/091708-02$01.50