

*Acta Cryst.* (1975). B31, 307

## Bis-( $\eta$ -cyclopentadienyl)- $\sigma$ -[(2-dimethylphenylphosphonium)ethyl]methyltungsten Hexafluorophosphate

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(Received 28 September 1974; accepted 30 September 1974)

**Abstract.**  $[(C_5H_5)_2W(CH_3)CH_2CH_2P(CH_3)_2C_6H_5](PF_6)_2$ ,  $C_{21}H_{28}F_6P_2W$ ,  $M = 640.3$ . Orthorhombic,  $Pbca$ , ( $D_{2h}^{12}$ , No. 61),  $a = 12.286$  (7),  $b = 40.813$  (18),  $c = 18.302$  (8) Å,  $U = 9177.5$  Å<sup>3</sup>,  $D_x = 1.87$  g cm<sup>-3</sup>,  $D_c = 1.85$  g cm<sup>-3</sup> for  $Z = 16$ . Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 55$  cm<sup>-1</sup>.

**Introduction.** The dark yellow material was provided by Mr N. J. Cooper and Dr M. L. H. Green (Cooper & Green, 1974). The crystals, thin plates perpendicular to [010], were mounted in nitrogen-filled Lindemann glass capillary tubes. After survey photography by oscillation and Weissenberg techniques the selected crystal (dimensions approximately  $0.2 \times 0.5 \times 0.02$  mm) was set up on a Hilger and Watts PDP8-controlled four-circle diffractometer and cell dimensions and orientation matrix obtained by a least-squares fit to the setting angles of 20 reflexions.

The intensities of each independent reflexion with  $\sin \theta/\lambda < 0.53$  were measured with an  $\omega/2\theta$  scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970). Mo  $K\alpha$  radiation from a graphite monochromator was used. Reflexions with intensity less than  $3\sigma$ , where  $\sigma$  is the standard deviation based on simple counting statistics, and those whose apparent centre was more than  $0.2^\circ$  from the predicted position were not included in subsequent calculations. Since mean intensity decreased rather rapidly with Bragg angle the resulting set of observed reflexions represented a relatively small fraction of the accessible sphere; even so, 3120 independent structure amplitudes were obtained. Lorentz and polarization corrections were applied and the empirical method of North, Phillips & Mathews (1968) was used in an attempt to correct for the substantial absorption effects arising from the crystal composition and habit.

The structure was solved by Patterson and Fourier techniques; no attempt was made to locate hydrogen atoms. Refinement was by the least-squares method with a large-block approximation to the normal matrix: a  $2 \times 2$  block was calculated from the derivatives of the scale and dummy overall temperature factor, four blocks from those of the positional parameters of the two independent cations and two anions, and a further four from those of the corresponding temperature factors. Tungsten, phosphorus and fluorine atoms were permitted anisotropic temperature factors, but the carbon atoms were refined isotropically. Each reflexion was assigned a weight according to the expression  $w^{-1} = 1 + \{(|F_o| - 162)/260\}^2$  and the final  $R$  was 0.056. All calculations were performed on the Oxford University ICL 1906A computer (Carruthers &

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
W(1)	4217 (1)	1985.1 (2)	4404.3 (5)	
P(1)	2409 (5)	1120 (1)	3015 (3)	
C(1)	3824 (18)	1508 (5)	3850 (11)	4 (1)
C(2)	2947 (17)	1517 (5)	3250 (11)	4 (1)
C(3)	1550 (22)	1162 (7)	2217 (14)	6 (1)
C(4)	1569 (19)	965 (6)	3744 (12)	5 (1)
C(5)	5366 (22)	1622 (7)	4914 (15)	6 (1)
C(11)	5232 (23)	2012 (7)	3326 (14)	7 (1)
C(12)	4361 (23)	2217 (6)	3270 (14)	6 (1)
C(13)	4543 (23)	2472 (7)	3824 (15)	7 (1)
C(14)	5531 (23)	2383 (7)	4213 (15)	7 (1)
C(15)	5890 (28)	2095 (8)	3848 (17)	9 (1)
C(21)	2570 (21)	1819 (6)	4965 (12)	5 (1)
C(22)	3345 (23)	1822 (7)	5503 (16)	7 (1)
C(23)	3751 (22)	2167 (7)	5552 (15)	6 (1)
C(24)	3135 (21)	2355 (6)	4995 (13)	6 (1)
C(25)	2427 (21)	2114 (5)	4627 (12)	5 (1)
C(31)	3467 (16)	811 (5)	2863 (11)	3 (1)
C(32)	4040 (20)	704 (6)	3471 (12)	5 (1)
C(33)	4806 (24)	465 (8)	3383 (16)	7 (1)
C(34)	4961 (23)	319 (7)	2692 (14)	6 (1)
C(35)	4386 (24)	421 (7)	2091 (15)	7 (1)
C(36)	3629 (20)	687 (6)	2172 (13)	5 (1)
W(2)	2590 (1)	4520.5 (2)	4090.5 (5)	
P(2)	4360 (5)	3515 (1)	3291 (3)	
C(41)	2882 (19)	4019 (6)	3592 (12)	5 (1)
C(42)	3906 (19)	3844 (5)	3873 (11)	4 (1)
C(43)	4833 (22)	3685 (6)	2440 (15)	6 (1)
C(44)	5484 (21)	3317 (6)	3736 (13)	6 (1)
C(45)	1105 (24)	4454 (7)	3362 (16)	7 (1)
C(51)	3920 (25)	4610 (7)	3167 (16)	8 (1)
C(52)	4343 (27)	4715 (8)	3833 (17)	8 (1)
C(53)	3664 (24)	4973 (8)	4114 (16)	8 (1)
C(54)	2790 (26)	5023 (8)	3558 (17)	8 (1)
C(55)	3041 (27)	4785 (8)	2987 (18)	9 (1)
C(61)	1989 (24)	4151 (17)	4987 (15)	7 (1)
C(62)	1157 (27)	4369 (8)	4882 (17)	8 (1)
C(63)	1545 (28)	4700 (8)	5067 (18)	9 (1)
C(64)	2623 (22)	4670 (6)	5269 (13)	6 (1)
C(65)	2982 (22)	4332 (7)	5224 (14)	6 (1)
C(71)	3296 (17)	3224 (5)	3121 (12)	4 (1)
C(72)	2514 (22)	3151 (6)	3659 (12)	5 (1)
C(73)	1753 (20)	2907 (6)	3551 (13)	5 (1)
C(74)	1713 (21)	2736 (6)	2893 (14)	6 (1)
C(75)	2492 (25)	2799 (7)	2359 (15)	7 (1)
C(76)	3282 (20)	3042 (6)	2452 (14)	5 (1)
P(3)	4248 (5)	1748 (2)	1030 (3)	
F(11)	5013 (17)	1539 (5)	533 (10)	
F(12)	3502 (16)	1955 (6)	1536 (10)	
F(13)	5036 (33)	1696 (10)	1608 (14)	
F(14)	3509 (23)	1822 (9)	417 (13)	
F(15)	4838 (26)	2058 (10)	806 (30)	
F(16)	3677 (34)	1455 (7)	1233 (26)	
P(4)	2464 (6)	4244 (2)	897 (4)	
F(21)	1607 (22)	4166 (9)	1480 (16)	
F(22)	3268 (25)	4156 (13)	1418 (16)	
F(23)	3142 (28)	4324 (14)	263 (15)	
F(24)	2358 (59)	4583 (8)	1208 (18)	
F(25)	1581 (30)	4377 (13)	401 (16)	
F(26)	2312 (57)	3942 (7)	529 (15)	

Table 2. *Anisotropic temperature factor components*

The temperature factor has the form  $\exp \{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\}$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
W(1)	0.0250 (4)	0.0236 (4)	0.0453 (4)	-0.0059 (4)	-0.0013 (4)	-0.0019 (4)
W(2)	0.0386 (5)	0.0257 (4)	0.0506 (5)	-0.0002 (4)	0.0107 (5)	-0.0054 (4)
P(1)	0.035 (3)	0.028 (3)	0.042 (3)	-0.002 (2)	-0.004 (3)	-0.004 (3)
P(2)	0.046 (4)	0.036 (3)	0.047 (3)	0.003 (3)	0.003 (3)	0.006 (3)
P(3)	0.038 (4)	0.076 (5)	0.048 (4)	0.010 (3)	0.001 (3)	0.014 (4)
P(4)	0.056 (4)	0.078 (5)	0.055 (4)	-0.005 (4)	-0.004 (4)	-0.009 (4)
F(11)	0.13 (2)	0.15 (2)	0.08 (1)	-0.00 (1)	0.02 (1)	0.10 (2)
F(12)	0.11 (2)	0.15 (2)	0.09 (1)	-0.02 (1)	0.01 (1)	0.06 (1)
F(13)	0.35 (5)	0.34 (5)	0.12 (2)	-0.11 (3)	-0.13 (3)	0.27 (4)
F(14)	0.18 (3)	0.32 (4)	0.11 (2)	-0.05 (2)	-0.06 (2)	0.14 (3)
F(15)	0.14 (3)	0.21 (4)	0.59 (8)	0.01 (4)	0.17 (4)	-0.05 (3)
F(16)	0.33 (5)	0.09 (2)	0.49 (6)	-0.00 (3)	0.27 (5)	-0.06 (2)
F(21)	0.15 (3)	0.27 (4)	0.17 (4)	0.03 (3)	0.07 (2)	-0.08 (3)
F(22)	0.18 (3)	0.57 (8)	0.13 (2)	0.09 (4)	-0.05 (2)	0.15 (4)
F(23)	0.20 (3)	0.51 (8)	0.11 (2)	0.02 (3)	0.06 (2)	-0.10 (4)
F(24)	0.72 (9)	0.17 (3)	0.15 (3)	-0.03 (2)	-0.01 (5)	-0.17 (5)
F(25)	0.22 (4)	0.53 (7)	0.12 (2)	-0.04 (3)	-0.04 (2)	0.20 (4)
F(26)	0.80 (9)	0.10 (2)	0.12 (2)	-0.01 (2)	0.05 (5)	0.02 (4)

Rollett, 1973). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Tables 1 and 2 list the final atomic parameters.\*

\* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30695 (37 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances (Å) and bond angles (°)*

## Cation I

W(1)-C(1)	2.25 (2)	W(1)-C(5)	2.25 (3)
W(1)-C(11)	2.24 (3)	W(1)-C(21)	2.37 (3)
W(1)-C(12)	2.29 (3)	W(1)-C(22)	2.37 (3)
W(1)-C(13)	2.29 (3)	W(1)-C(23)	2.30 (3)
W(1)-C(14)	2.32 (3)	W(1)-C(24)	2.28 (3)
W(1)-C(15)	2.34 (3)	W(1)-C(25)	2.30 (3)
C(1)-C(2)	1.54 (3)	C(11)-C(12)	1.36 (4)
P(1)-C(2)	1.80 (2)	C(12)-C(13)	1.47 (4)
P(1)-C(3)	1.81 (3)	C(13)-C(14)	1.46 (4)
P(1)-C(4)	1.80 (2)	C(14)-C(15)	1.42 (4)
P(1)-C(31)	1.83 (2)	C(15)-C(11)	1.30 (4)
C(31)-C(32)	1.39 (3)	C(21)-C(22)	1.37 (3)
C(32)-C(33)	1.37 (4)	C(22)-C(23)	1.49 (4)
C(33)-C(34)	1.41 (4)	C(23)-C(24)	1.49 (4)
C(34)-C(35)	1.37 (4)	C(24)-C(25)	1.47 (3)
C(35)-C(36)	1.44 (4)	C(25)-C(21)	1.36 (3)
C(36)-C(31)	1.38 (3)		
C(1)-W(1)-C(5)	75.6 (9)	W(1)-C(1)-C(2)	117 (3)
C(2)-P(1)-C(3)	109 (3)	C(1)-C(2)-P(1)	114 (3)
C(2)-P(1)-C(4)	110 (2)		
C(2)-P(1)-C(31)	113 (2)	C(31)-C(32)-C(33)	119 (5)
C(3)-P(1)-C(4)	107 (2)	C(32)-C(33)-C(34)	120 (5)
C(3)-P(1)-C(31)	111 (2)	C(33)-C(34)-C(35)	121 (5)
C(4)-P(1)-C(31)	106 (2)	C(34)-C(35)-C(36)	119 (5)
P(1)-C(31)-C(32)	117 (4)	C(35)-C(36)-C(31)	118 (5)
P(1)-C(31)-C(36)	120 (3)	C(36)-C(31)-C(32)	123 (4)
C(11)-C(12)-C(13)	105 (5)	C(21)-C(22)-C(23)	106 (5)
C(12)-C(13)-C(14)	107 (6)	C(22)-C(23)-C(24)	106 (5)
C(13)-C(14)-C(15)	104 (6)	C(23)-C(24)-C(25)	106 (5)
C(14)-C(15)-C(11)	112 (6)	C(24)-C(25)-C(21)	108 (5)
C(15)-C(11)-C(12)	113 (6)	C(25)-C(21)-C(22)	114 (5)

Table 3 (cont.)

## Cation II

W(2)-C(41)	2.27 (2)	W(2)-C(45)	2.28 (3)
W(2)-C(51)	2.38 (3)	W(2)-C(61)	2.35 (3)
W(2)-C(52)	2.34 (3)	W(2)-C(62)	2.36 (3)
W(2)-C(53)	2.27 (3)	W(2)-C(63)	2.32 (3)
W(2)-C(54)	2.28 (3)	W(2)-C(64)	2.24 (2)
W(2)-C(55)	2.36 (3)	W(2)-C(65)	2.26 (3)
C(41)-C(42)	1.54 (3)	C(51)-C(52)	1.39 (4)
P(2)-C(42)	1.80 (2)	C(52)-C(53)	1.44 (4)
P(2)-C(43)	1.80 (3)	C(53)-C(54)	1.49 (4)
P(2)-C(44)	1.80 (3)	C(54)-C(55)	1.46 (4)
P(2)-C(71)	1.79 (2)	C(55)-C(51)	1.34 (4)
C(71)-C(72)	1.41 (3)	C(61)-C(62)	1.37 (4)
C(72)-C(73)	1.38 (3)	C(62)-C(63)	1.48 (4)
C(73)-C(74)	1.39 (3)	C(63)-C(64)	1.38 (4)
C(74)-C(75)	1.39 (4)	C(64)-C(65)	1.45 (3)
C(75)-C(76)	1.40 (4)	C(65)-C(61)	1.49 (4)
C(76)-C(71)	1.43 (3)		
C(41)-W(2)-C(45)	77.5 (9)	W(2)-C(41)-C(42)	115 (4)
C(42)-P(2)-C(43)	109 (3)	C(41)-C(42)-P(2)	114 (4)
C(42)-P(2)-C(44)	108 (3)		
C(42)-P(2)-C(71)	112 (2)	C(71)-C(72)-C(73)	121 (4)
C(43)-P(2)-C(44)	108 (3)	C(72)-C(73)-C(74)	121 (4)
C(43)-P(2)-C(71)	110 (2)	C(73)-C(74)-C(75)	119 (5)
C(44)-P(2)-C(71)	110 (2)	C(74)-C(75)-C(76)	122 (5)
P(2)-C(71)-C(72)	121 (4)	C(75)-C(76)-C(71)	119 (5)
P(2)-C(71)-C(76)	120 (4)	C(76)-C(71)-C(72)	119 (4)
C(51)-C(52)-C(53)	109 (6)	C(61)-C(62)-C(63)	109 (6)
C(52)-C(53)-C(54)	106 (6)	C(62)-C(63)-C(64)	107 (6)
C(53)-C(54)-C(55)	104 (6)	C(63)-C(64)-C(65)	111 (5)
C(54)-C(55)-C(51)	111 (6)	C(64)-C(65)-C(61)	104 (5)
C(55)-C(51)-C(52)	111 (6)	C(65)-C(61)-C(62)	109 (5)

## Anion I

P(3)-F(11)	1.56 (2)	P(3)-F(14)	1.47 (2)
P(3)-F(12)	1.55 (2)	P(3)-F(15)	1.52 (3)
P(3)-F(13)	1.45 (2)	P(3)-F(16)	1.43 (3)
F(11)-P(3)-F(12)	179 (1)	F(12)-P(3)-F(16)	91 (4)
F(11)-P(3)-F(13)	87 (1)	F(13)-P(3)-F(14)	175 (3)
F(11)-P(3)-F(14)	92 (4)	F(13)-P(3)-F(15)	90 (3)
F(11)-P(3)-F(15)	91 (5)	F(13)-P(3)-F(16)	91 (5)
F(11)-P(3)-F(16)	89 (2)	F(14)-P(3)-F(15)	85 (2)
F(12)-P(3)-F(13)	92 (4)	F(14)-P(3)-F(16)	94 (5)
F(12)-P(3)-F(14)	89 (1)	F(15)-P(3)-F(16)	179 (3)
F(12)-P(3)-F(15)	89 (2)		

Table 3 (cont.)

Anion II			
P(4)—F(21)	1.53 (2)	P(4)—F(24)	1.50 (4)
P(4)—F(22)	1.42 (2)	P(4)—F(25)	1.51 (3)
P(4)—F(23)	1.47 (3)	P(4)—F(26)	1.42 (3)
F(21)—P(4)—F(22)	88 (2)	F(22)—P(4)—F(26)	101 (4)
F(21)—P(4)—F(23)	171 (2)	F(23)—P(4)—F(24)	98 (5)
F(21)—P(4)—F(24)	82 (2)	F(23)—P(4)—F(25)	82 (2)
F(21)—P(4)—P(25)	90 (2)	F(23)—P(4)—F(26)	84 (3)
F(21)—P(4)—F(26)	93 (6)	F(24)—P(4)—F(25)	81 (3)
F(22)—P(4)—F(23)	101 (4)	F(24)—P(4)—F(26)	166 (4)
F(22)—P(4)—F(24)	92 (5)	F(25)—P(4)—F(26)	86 (3)
F(22)—P(4)—F(25)	173 (3)		

Table 3 lists interatomic distances and interbond angles. Fig. 1 shows a projection of one of the crystallographically independent cations; the other consists of W(2) and P(2) together with carbon atoms whose serial numbers are obtained by adding 40 to the corresponding ones in the figure.

**Discussion.** The material was obtained from the reaction of dimethyl phenyl phosphine with bis-( $\eta$ -cyclopentadienyl)ethylenemethyltungsten hexafluorophosphate,  $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{CH}_3]\text{PF}_6$  and the X-ray investigation was undertaken to characterize the unexpected product, the formation of which has important mechanistic consequences (Cooper & Green, 1974).

The structure consists of discrete organometallic cations and hexafluorophosphate anions, the asymmetric unit consisting of two formula units. The geometry of the two independent cations is the same

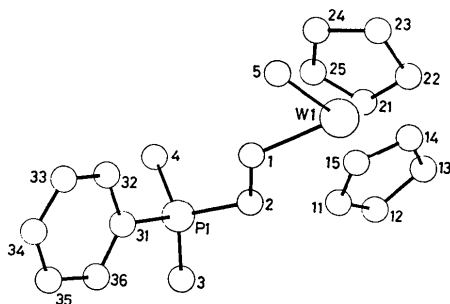


Fig. 1. One of the cations in projection down *a*. For clarity, carbon atoms are labelled by their serial number only.

within experimental error and shows no unexpected features. The mean W—C  $\sigma$ -bond length of 2.26 Å and the mean CH<sub>3</sub>—W—CH<sub>2</sub> angle of 77.5° may be compared with the corresponding values of 2.30 Å and 75.3° in bis-( $\eta$ -cyclopentadienyl) bis-(3,5-dimethylbenzyl)tungsten(IV) (Elmitt, Green, Forder, Jefferson & Prout, 1974). For further comparison, the mean W—CH<sub>3</sub> bond length in tetramethyl-bis-(*N*-methyl-*N*-nitrosohydroxylamino)tungsten(VI) is 2.20 Å (Fletcher, Shortland, Skapski & Wilkinson, 1972). The CH<sub>3</sub>—W—CH<sub>2</sub> angle is also consistent with corresponding values in ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoX<sub>2</sub> complexes with *d*<sup>2</sup> configurations (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The tungsten atom lies, on average, 1.99 Å from the mean planes of the cyclopentadienyl rings and the mean angle between ring normals is 134° — very close to the values observed in the compounds ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>W(SPh)<sub>2</sub>M(CO)<sub>4</sub> (M = Cr, Mo, W) (Prout & Rees, 1974). Projections on to the W(1)C(1)C(5) and W(2)C(41)C(45) planes show that the cyclopentadienyl rings adopt an almost eclipsed configuration in both cations.

As is usually observed with ions having spherical symmetry, the hexafluorophosphate groups have large temperature factors and show considerable apparent distortion.

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