Bis(η^5-cyclopentadienyl)(η-ethylene)methyltungsten Hexafluorophosphate

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Abstract. $[W(CH_3)(C_2H_4)(C_5H_5)_2]PF_6$, $M_r = 502 \cdot 09$, tetragonal, $a = 13 \cdot 941$ (8), $c = 14 \cdot 799$ (9) Å, $U = 2876$ Å^3, space group $I4/mcm$, $Z = 8$, $D_c = 2 \cdot 3$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å), $\mu = 86 \cdot 0$ cm^{-1}, for 536 reflections $R = 0 \cdot 037$, $R_w = 0 \cdot 049$. The bis(η^5-cyclopentadienyl)(η-ethylene)methyltungsten cation itself has crystallographic $2mm$ symmetry with the W atom lying on the twofold axis. The methyl and the ethylene groups are disordered. The distance W–C(4)(methyl) is $2 \cdot 26$ (2), and W–C(4)(ethylene) and W–C(5)(ethylene) are $2 \cdot 26$ (2) and $2 \cdot 44$ (3) Å respectively. The length of the normal from W to the cyclopentadienyl ring is $1 \cdot 997$ Å, and the angle between the two normals is $134 \cdot 9°$.

Introduction. The title compound was synthesized by reacting the neutral complex (η^5-C_5H_5)$_2$W(CH$_2$CH$_2$) with methyl iodide, and treating the product with ammonium hexafluorophosphate (Benfield, Cooper & Green, 1974). The formation of a tungsten methylene hydride derivative, from the reaction of the title compound with dimethyl(phenyl)phosphine, provided evidence for a reversible α-hydride elimination (Cooper & Green, 1974). Further elegant investigation of this system has been carried out (Canestrari & Green, 1979) and the interesting reactions of the title compound led us to investigate its structural features.

Crystals of the title compound were supplied by Drs M. L. H. Green and M. Canestrari; one with dimensions $0 \cdot 1 \times 0 \cdot 2 \times 0 \cdot 2$ mm was sealed in a thin-walled capillary in a nitrogen atmosphere for data collection on an Enraf–Nonius CAD4-F diffractometer. With Mo $K\alpha$ radiation from a graphite monochromator, the unit-cell dimensions and orientation matrix were obtained by least squares from the setting angles of 25 reflections. The intensities of the reflections with $\theta \leq 25°$ were measured in the $\omega/2\theta$ scan mode with a variable scan rate and ω-scan angle of $(1 \cdot 0 + 0 \cdot 35 \tan \theta)°$. 1894 independent reflections were measured and 536 of these with $I \geq 3\sigma(I)$ were used in the structure analysis. The observed reflections were corrected for Lorentz and polarization factors but not for absorption.

The position of the W atom was deduced from an unsharpened Patterson map; the subsequent calculation of a Fourier map allowed the location of the C atoms forming the η-cyclopentadienyl rings and the two crystallographically independent hexafluorophosphate groups. A difference Fourier map phased on atoms found above, in addition to a slant difference Fourier map at $z = 0$, revealed the positions of the disordered methyl and ethylene C atoms. No attempt was made to locate the H atoms. The structure was refined by full-matrix least squares first with isotropic and then anisotropic thermal parameters, and the refinement converged at $R = 0 \cdot 037$, $R_w = 0 \cdot 049$. Weights were computed from the Chebyshev series $w = 28 \cdot 87t_0(x) + 38 \cdot 93t_1(x) + 11 \cdot 89t_2(x)^{-1}$, where $(x) = (F_o/F_{max})$ (Carruthers & Watkin, 1979). Data reduction and structure refinement were performed with *CRYSTALS* (Carruthers & Watkin, 1980) in Oxford. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Positional and equivalent isotropic thermal parameters are given in Table 1;‡ selected interatomic distances and interbond angles with e.s.d.'s calculated from the variance–covariance matrix are listed in Table 2.

Discussion. The structure consists of discrete organometallic cations and PF$_6^-$ anions; a perspective view of the bis(η^5-cyclopentadienyl)(η-ethylene)methyl cation is shown in Fig. 1. The space group imposes $2mm$ symmetry on the site of the W atom. The methyl and ethylene groups are located along with W in a mirror plane, and are disordered over two positions as required by the second mirror plane. The eclipsed conformation of the planar cyclopentadienyl rings is also dictated by the symmetry. The length of the normal from W to the cyclopentadienyl ring is $1 \cdot 997$ Å and the angle between the ring normals is $134 \cdot 9°$, close to the values $1 \cdot 99$ Å and $134°$ observed in the bis(η-cyclopentadienyl)-σ-{2-[dimethyl(phenyl)phosphonio]ethyl}methyltungsten cation (Forder, Gale &

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Table 1. *Fractional atomic coordinates (with e.s.d.'s in parentheses) and equivalent isotropic temperature factors (mean e.s.d.* 0.007 Å^2)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$, where U_1, U_2 and U_3 are the mean square displacements (Å^2) along each of the principal axes of the thermal ellipsoid.

	x	y	z	U_{eq} (Å^2)
W	0·22200(4)	0·72200 (4)	0·0	0·0315
C(1)	0·2476 (9)	0·6768 (9)	0·1519 (7)	0·0484
C(2)	0·3321 (9)	0·7180 (8)	0·1158 (8)	0·0547
C(3)	0·3135 (7)	0·8135 (7)	0·0966 (9)	0·0422
C(4)	0·1971 (14)	0·5617 (9)	0·0	0·0516
C(5)	0·3005 (23)	0·5654 (20)	0·0	0·0488
P(1)	0·0	0·0	0·25	0·0384
P(2)	0·5	0·0	0·25	0·0390
F(11)	0·1129 (6)	0·0	0·25	0·0740
F(12)	0·0	0·0	0·3560 (10)	0·0876
F(21)	0·5	0·0	0·3576 (9)	0·0812
F(22)	0·3862 (6)	0·0	0·25	0·0803

Table 2. *Bond distances* (Å) *and interbond angles* (°) *with e.s.d.'s in parentheses*

W—C(1)	2·36 (1)	C(1)—C(1^i)	1·40 (3)
W—C(2)	2·30 (2)	C(4)—C(5)	1·44 (4)
W—C(3)	2·30 (2)	P(1)—F(11)	1·574 (8)
W—C(4)	2·26 (2)	P(1)—F(12)	1·568 (15)
W—C(5)	2·44 (3)	P(2)—F(21)	1·593 (14)
C(1)—C(2)	1·41 (2)	P(2)—F(22)	1·586 (8)
C(2)—C(3)	1·39 (2)		

C(1^i)—C(1)—C(2)	107·5 (8)	C(4)—W—C(4^i)	72·3 (10)
C(1)—C(2)—C(3)	108·2 (12)	C(5)—W—C(5^i)	143·3 (17)
C(2)—C(3)—C(2^i)	108·4 (15)	C(5)—W—C(4^i)	107·8 (10)

Symmetry code: (i) $-\frac{1}{2} + y, \frac{1}{2} + x, z$.

Prout, 1975) and 2·004 Å and 137° in (1,2-benzene-dithiolato)bis(η-cyclopentadienyl)tungsten (Debaerde-maeker & Kutoglu, 1973). The ten W—C(π) bond distances, which range from 2·30 (2) to 2·36 (2) Å, mean 2·32 Å, are not significantly different in length. These values are comparable with 2·246 (7)–2·392 (7) Å found for bis(η-cyclopentadienyl)bis(3,5-dimethylbenzyl)tungsten (Forder, Jefferson & Prout, 1975) and 2·24 (2)–2·37 (3) Å for bis(η-cyclopenta-dienyl)-σ-{2-[dimethyl(phenyl)phosphonio]ethyl}meth-yltungsten (Forder, Gale & Prout, 1975). The angle at W between the normal to the cyclo-pentadienyl ring and the vector to the ring-plane centroid is only 3·6°. The W—C(4)(methyl) distance 2·26 (2) Å is the same as the mean W—C(σ), 2·26 Å, in the bis(η-cyclopentadienyl)-σ-{2-[dimethyl(phenyl)-phosphonio]ethyl}methyltungsten cation (Forder, Gale & Prout, 1975) and consistent with the lengths of 2·276 (7) and 2·291 (7) Å in bis(η-cyclopenta-dienyl)bis(3,5-dimethylbenzyl)tungsten (Forder, Jeffer-son & Prout, 1975), and with the Mo—C(σ) bond average, 2·291 (5) Å, found for MoMe$_2$(η^6-C$_6$H$_5$Me)-(PPhMe$_2$)$_2$ (Atwood, Hunter, Rogers, Carmona-Guzman & Wilkinson, 1979). The angle at W between
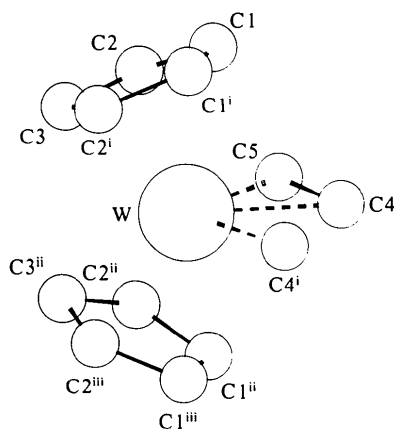

Fig. 1. A perspective view of the bis(η^5-cyclopentadienyl)(η-ethylene)methyltungsten cation. Symmetry code: (i) $-\frac{1}{2} + y, \frac{1}{2} + x, z$; (ii) $x,y,-z$; (iii) $-\frac{1}{2} + y, \frac{1}{2} + x, -z$.

the two disordered W—C(4) bonds, 72·3 (10)°, is comparable with the corresponding value, 75·3°, in bis(η-cyclopentadienyl)bis(3,5-dimethylbenzyl)tungsten (Forder, Jefferson & Prout, 1975), but less than the mean value, 77·5°, for the bis(η-cyclopenta-dienyl)-σ-{2-[dimethyl(phenyl)phosphonio]ethyl}meth-yltungsten cation (Forder, Gale & Prout, 1975). The two ethylene C atoms have significantly different bond lengths to W; 2·26 (2) for C(4) and 2·44 (3) Å for C(5). However, the disordered distribution of the ethylene group makes the importance of this difference unclear. The dimensions of the cyclopentadienyl residues are as expected.

There are two crystallographically distinct PF$_6^-$ ions, one of symmetry 42 at Wyckoff (a) and the other of symmetry $\bar{4}2m$ at Wyckoff (b).

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