

Acta Cryst. (1975). B31, 618**Bis-(η -cyclopentadienyl)bis-(3,5-dimethylbenzyl)tungsten**

BY ROGER A. FORDER, IAN W. JEFFERSON AND KEITH PROUT

Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England

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Abstract. $(C_5H_5)_2W[CH_2C_6H_3(CH_3)_2]_2$, $C_{28}H_{32}W$, $M = 552.5$. Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14). $a = 8.619$ (5), $b = 22.278$ (12), $c = 11.921$ (7) Å, $\beta = 95.0$ (1)°; $U = 2280.4$ Å³. $D_c = 1.61$ g cm⁻³ for $Z = 4$. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 54$ cm⁻¹.

Introduction. The orange material was provided by Mr K. Elmitt and Dr M. L. H. Green (Elmitt, Green, Forder, Jefferson & Prout, 1974). After survey photography by oscillation and Weissenberg techniques, a selected crystal (approximately $0.3 \times 0.3 \times 0.3$ mm) mounted in a nitrogen-filled glass capillary 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 17 reflexions.

The intensities of each independent reflexion with $\sin \theta/\lambda < 0.7$ were measured by an $\omega/2\theta$ scan with ordinate analysis (Watson, Shotton, Cox & Muirhead, 1970). Mo $K\alpha$ radiation from a graphite monochrom-

ator was used. Reflexions with $I < 3\sigma$, where σ is the standard deviation based on simple counting statistics, and those whose apparent centre was more than 0.14° from the predicted position were not included in subsequent calculations. Lorentz and polarization corrections were applied, together with an empirical absorption correction (North, Phillips & Mathews, 1968), to give a final set of 3586 independent observed structure amplitudes.

The structure was solved by Patterson and Fourier techniques. Difference syntheses permitted the location of some of the hydrogen atoms in their expected positions, but they were not included in the final model. Refinement employed the least-squares method with a large-block approximation to the normal matrix: a 2×2 block was calculated from the derivatives of the scale and dummy overall temperature factor, and three blocks from those of the atomic positional parameters, the diagonal elements of the anisotropic temperature factors, and the off-diagonal elements respectively.

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic temperature factor components ($\times 10^3$)

The temperature factor is given by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k lb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	5288.0 (2)	1564.4 (1)	930.4 (2)	24.2 (1)	24.7 (1)	30.1 (1)	-1.3 (1)	2.6 (1)	0.0 (1)
C(11)	5028 (8)	2101 (3)	-786 (5)	76 (4)	39 (3)	50 (3)	4 (3)	19 (3)	-5 (3)
C(12)	6636 (9)	2041 (3)	-356 (7)	68 (4)	51 (4)	91 (5)	11 (3)	40 (3)	-7 (3)
C(13)	6795 (9)	2371 (3)	712 (8)	69 (5)	43 (4)	122 (7)	9 (4)	6 (4)	-19 (3)
C(14)	5274 (10)	2598 (3)	907 (6)	110 (7)	33 (3)	72 (5)	-2 (3)	17 (4)	3 (3)
C(15)	4251 (9)	2435 (3)	-26 (6)	73 (4)	41 (3)	64 (4)	19 (3)	14 (3)	11 (3)
C(21)	6420 (7)	677 (3)	1784 (5)	49 (3)	50 (3)	51 (3)	8 (3)	-2 (3)	11 (3)
C(22)	7515 (8)	1147 (3)	1901 (6)	45 (3)	72 (4)	70 (4)	2 (3)	-14 (3)	13 (3)
C(23)	6889 (9)	1613 (3)	2558 (7)	60 (4)	70 (5)	69 (4)	-9 (3)	-24 (3)	7 (3)
C(24)	5366 (8)	1437 (3)	2821 (5)	61 (4)	61 (4)	38 (3)	-1 (3)	-7 (3)	9 (3)
C(25)	5098 (7)	851 (3)	2309 (5)	60 (4)	50 (3)	45 (3)	16 (2)	2 (3)	9 (3)
C(31)	4643 (7)	864 (3)	-420 (5)	45 (3)	43 (3)	42 (3)	-5 (2)	5 (2)	-4 (2)
C(32)	5731 (7)	741 (2)	-1318 (5)	60 (3)	36 (3)	40 (3)	-0 (2)	7 (2)	-1 (2)
C(33)	5204 (8)	828 (3)	-2448 (5)	82 (5)	38 (3)	43 (3)	-2 (2)	3 (3)	-2 (3)
C(34)	6167 (9)	705 (3)	-3319 (5)	98 (5)	39 (3)	44 (3)	-4 (3)	15 (3)	-3 (3)
C(35)	7668 (9)	495 (3)	-3051 (6)	79 (4)	48 (3)	61 (4)	-0 (3)	28 (3)	1 (3)
C(36)	8227 (8)	413 (3)	-1926 (6)	64 (4)	44 (3)	68 (4)	-2 (3)	22 (3)	-0 (3)
C(37)	7258 (7)	533 (3)	-1088 (5)	49 (3)	49 (3)	51 (3)	0 (3)	13 (2)	6 (3)
C(38)	5545 (13)	813 (4)	-4550 (6)	157 (9)	72 (5)	41 (4)	8 (3)	9 (4)	5 (5)
C(39)	9878 (9)	190 (4)	-1637 (7)	56 (4)	80 (5)	93 (5)	-6 (4)	22 (3)	14 (4)
C(41)	2652 (6)	1442 (3)	960 (5)	32 (3)	60 (3)	41 (3)	-6 (2)	5 (2)	1 (2)
C(42)	1892 (6)	1700 (3)	1937 (5)	31 (3)	57 (3)	45 (3)	-4 (3)	4 (2)	-2 (2)
C(43)	1479 (7)	2311 (3)	1976 (5)	40 (3)	63 (4)	55 (3)	-6 (3)	4 (3)	8 (3)
C(44)	760 (7)	2550 (3)	2886 (5)	44 (3)	68 (4)	51 (3)	-9 (3)	3 (3)	4 (3)
C(45)	427 (7)	2171 (4)	3750 (5)	39 (3)	85 (5)	48 (3)	-12 (3)	7 (2)	2 (3)
C(46)	794 (8)	1564 (3)	3744 (6)	44 (3)	85 (5)	48 (3)	-4 (3)	7 (3)	-11 (3)
C(47)	1529 (7)	1338 (3)	2833 (5)	41 (3)	64 (4)	49 (3)	0 (3)	7 (2)	-9 (3)
C(48)	348 (10)	3204 (4)	2893 (7)	87 (5)	74 (5)	76 (5)	-13 (4)	15 (4)	24 (4)
C(49)	366 (11)	1153 (5)	4678 (7)	96 (6)	115 (7)	68 (4)	18 (5)	36 (4)	-5 (5)

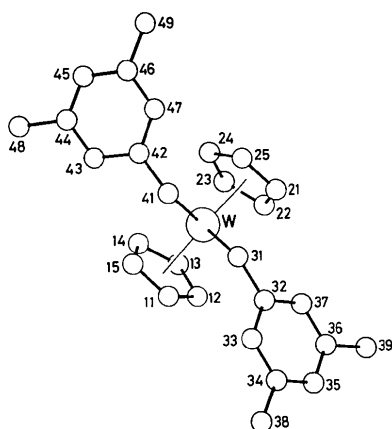


Fig. 1. The molecule in projection down the bisector of the C(31)-W-C(41) angle. For clarity, carbon atoms are labelled by their serial number only.

Table 2. Interatomic distances (Å) and bond angles (°)

$\sigma(\text{W}-\text{C})=0.007$, $\sigma(\text{C}-\text{C})=0.01$ Å. $\sigma(\text{C}-\text{W}-\text{C})=0.2$, $\sigma(\text{W}-\text{C}-\text{C})=1$, $\sigma(\text{C}-\text{C}-\text{C})=1.5^\circ$.

W—C(11)	2.363	W—C(21)	2.392
W—C(12)	2.267	W—C(22)	2.346
W—C(13)	2.246	W—C(23)	2.284
W—C(14)	2.302	W—C(24)	2.266
W—C(15)	2.384	W—C(25)	2.302
W—C(31)	2.276	W—C(41)	2.291
C(11)-C(12)	1.44	C(21)-C(22)	1.41
C(12)-C(13)	1.47	C(22)-C(23)	1.43
C(13)-C(14)	1.44	C(23)-C(24)	1.43
C(14)-C(15)	1.41	C(24)-C(25)	1.45
C(15)-C(11)	1.39	C(25)-C(21)	1.40
C(31)-C(32)	1.51	C(41)-C(42)	1.50
C(32)-C(33)	1.40	C(42)-C(43)	1.41
C(33)-C(34)	1.41	C(43)-C(44)	1.40
C(34)-C(35)	1.39	C(44)-C(45)	1.38
C(34)-C(38)	1.54	C(44)-C(48)	1.50
C(35)-C(36)	1.40	C(45)-C(46)	1.39
C(36)-C(37)	1.38	C(46)-C(47)	1.40
C(36)-C(39)	1.52	C(46)-C(49)	1.51
C(37)-C(32)	1.40	C(47)-C(42)	1.39
C(31)-W—C(41)	75.4	C(21)-C(22)-C(23)	108
C(11)-C(12)-C(13)	106	C(22)-C(23)-C(24)	108
C(12)-C(13)-C(14)	107	C(23)-C(24)-C(25)	106
C(13)-C(14)-C(15)	107	C(24)-C(25)-C(21)	109
C(14)-C(15)-C(11)	110	C(25)-C(21)-C(22)	108
C(15)-C(11)-C(12)	109	W—C(41)-C(42)	118
W—C(31)-C(32)	120	C(41)-C(42)-C(43)	122
C(31)-C(32)-C(33)	119	C(41)-C(42)-C(47)	121
C(31)-C(32)-C(37)	124	C(43)-C(42)-C(47)	117
C(33)-C(32)-C(34)	117	C(42)-C(43)-C(44)	122
C(32)-C(33)-C(34)	121	C(43)-C(44)-C(45)	119
C(33)-C(34)-C(35)	119	C(43)-C(44)-C(48)	120
C(33)-C(34)-C(38)	120	C(45)-C(44)-C(48)	122
C(35)-C(34)-C(38)	121	C(44)-C(45)-C(46)	122
C(34)-C(35)-C(36)	120	C(45)-C(46)-C(47)	118
C(35)-C(36)-C(37)	119	C(45)-C(46)-C(49)	121
C(35)-C(36)-C(39)	120	C(47)-C(46)-C(49)	121
C(37)-C(36)-C(39)	121	C(46)-C(47)-C(42)	122
C(36)-C(37)-C(32)	123		

Each reflexion was assigned a weight according to the expression

$$w^{-1} = 1 + \{(F_o - 36)/24\}^2$$

and the final R was 0.032. All calculations were performed on the Oxford University ICL 1906A computer (Carruthers & Rollett, 1973). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic parameters are given in Table 1.* Table 2 lists interatomic distances and interbond angles.

Irradiation of $(\eta\text{-C}_5\text{H}_5)\text{WH}_2$ in mesitylene (Elmitt *et al.*, 1974) gives an orange compound which is slightly soluble in, and may be recrystallized from, benzene. To characterize this compound unambiguously an X-ray structure analysis was undertaken. The compound proved to be $(\eta\text{-C}_5\text{H}_5)_2\text{W}[\text{CH}_2(3,5\text{-Me}_2\text{C}_6\text{H}_3)]_2$ and the reaction is apparently the first example (along with the corresponding *p*-xylene derivative) of the direct insertion of a transition metal into an uncoordinated saturated C-H group.

The structure of the molecule, seen in Fig. 1 in projection down the bisection of the C(31)-W-C(41) angle, is as would be expected from the known structures of bent d^2 $(\eta\text{-C}_5\text{H}_5)\text{MX}_2$ systems (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974) and is the most symmetrical structure compatible with the steric limitations of the system. However, the inequivalence of the four methylene hydrogen atoms, suggested by the ^1H n.m.r. spectrum in solution, is confirmed by the conformation of the carbon skeleton in the solid-state structure although these hydrogen atoms are not located. If the hydrogen atoms were to be equivalent then in Fig. 1 C(32), C(31), C(41) and C(42) should lie on a straight line.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30747 (31 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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