

The Crystal and Molecular Structures of *trans*-Di- μ -(σ : η^5 -cyclopentadienyl)-bis(η^5 -cyclopentadienyl)dihydridoditungsten and the *cis* and *trans* Isomers of Di- μ -(σ : η^5 -cyclopentadienyl)-bis(η^5 -cyclopentadienyl)(hydrido)trimethylsilylmethylditungsten

BY CLAIRE COULDWELL AND KEITH PROUT

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

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Abstract

The crystal structures of *trans*- $\{(\eta^5\text{-C}_5\text{H}_5)(\text{H})\text{W}[\mu\text{-}(\sigma\text{:}\eta^5\text{-C}_5\text{H}_4)_2\text{W}(\text{H})(\eta^5\text{-C}_5\text{H}_5)]\}$, $\text{C}_{20}\text{H}_{20}\text{W}_2$ (I) [triclinic, $a = 6.058$ (1), $b = 7.679$ (3), $c = 8.492$ (2) Å, $\alpha = 92.53$ (2), $\beta = 101.27$ (2), $\gamma = 100.95$ (2)°, $Z = 1$, space group $P\bar{1}$, 1937 reflexions, $R_w = 0.079$], *cis*- $\{(\eta^5\text{-C}_5\text{H}_5)[\text{CH}_2\text{Si}(\text{CH}_3)_3]\text{W}[\mu\text{-}(\sigma\text{:}\eta^5\text{-C}_5\text{H}_4)_2\text{W}(\text{H})(\eta^5\text{-C}_5\text{H}_5)]\}$, $\text{C}_{24}\text{H}_{30}\text{SiW}_2$ (II) [monoclinic, $a = 8.756$ (8), $b = 23.223$ (18), $c = 10.672$ (5) Å, $\beta = 100.24$ (6)°, $Z = 4$, space group $P2_1/n$, 4091 reflexions, $R_w = 0.132$], and *trans*- $\{(\eta^5\text{-C}_5\text{H}_5)[\text{CH}_2\text{Si}(\text{CH}_3)_3]\text{W}[\mu\text{-}(\sigma\text{:}\eta^5\text{-C}_5\text{H}_4)_2\text{W}(\text{H})(\eta^5\text{-C}_5\text{H}_5)]\}$, $\text{C}_{24}\text{H}_{30}\text{SiW}_2$ (III) [monoclinic, $a = 16.530$ (2), $b = 7.759$ (1), $c = 18.208$ (2) Å, $\beta = 110.55$ (1)°, $Z = 4$, space group $P2_1/c$, 2484 reflexions, $R_w = 0.035$], have been determined. The bis[bis(η^5 -cyclopentadienyl)tungsten] skeleton is similar in each structure. The W atoms, separated by (I) 3.811 (1), (II) 3.816 (1) and (III) 3.859 (1) Å, are bridged by C atoms provided by the adjacent η^5 -cyclopentadienyl rings, which are therefore formulated as C_5H_4 . The coordination sphere about each W atom is completed either by a $\text{CH}_2\text{Si}(\text{CH}_3)_3$ group [W(1) in (II) and (III)] or by a hydrido ligand [W(1), and W(2) in (II) and (III)].

Introduction

During investigations of the photoinduced synthesis of binuclear tungstenocene derivatives it was found to be possible to achieve insertion of W into saturated C–H bonds. Irradiation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ in diethyl ether yields *trans*- $\{(\eta^5\text{-C}_5\text{H}_5)[\mu\text{-}(\sigma\text{:}\eta^5\text{-C}_5\text{H}_4)]\text{WH}\}_2$ (Berry, Davies & Green, 1978). Irradiation in tetramethylsilane gives isomeric dimers of stoichiometry $\text{C}_{24}\text{H}_{30}\text{SiW}_2$ containing the $\text{CH}_2\text{Si}(\text{CH}_3)_3$ group, and a preliminary account of one of these has appeared (Green, Berry, Couldwell & Prout, 1977). In that publication it was suggested that the less soluble isomer has the *trans* configuration. However, on closer examination and comparison with the other isomer it is found that the less soluble isomer is better described as

having a *cis* configuration. In this paper we report the structures of these three binuclear tungstenocene derivatives in detail.

Experimental

Small orange-brown plate-like crystals of all three compounds were provided by Miss M. Berry and Dr M. L. H. Green. The compounds are sensitive to air and moisture and were sealed under dry nitrogen in glass capillaries. It was not possible to measure their densities.

After survey photography by precession techniques, the crystals were set up on a Nonius CAD-4F PDP-8-controlled κ -geometry diffractometer which used Mo $K\alpha$ radiation from a graphite monochromator. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions.

Crystal data

(a) Compound (I): $\text{C}_{20}\text{H}_{20}\text{W}_2$, $M_r = 628.0$, triclinic, $a = 6.058$ (1), $b = 7.679$ (3), $c = 8.492$ (2) Å, $\alpha = 92.53$ (2), $\beta = 101.27$ (2), $\gamma = 100.95$ (2)°, $U = 379.0$ Å³. Space group $P\bar{1}$ or $P1$; $P\bar{1}$ from structure analysis. $D_c = 2.75$ Mg m⁻³ for $Z = 1$. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 15.5$ mm⁻¹. 1937 independent reflexions, $I > 3\sigma(I)$. * No absorption correction.

The intensities of each independent reflexion with $\sin \theta/\lambda < 0.70$ Å⁻¹ were measured with an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $1.20 + 0.35 \tan \theta$ °.

(b) Compound (II): $\text{C}_{24}\text{H}_{30}\text{SiW}_2$, $M_r = 714.3$, monoclinic, $a = 8.756$ (8), $b = 23.223$ (18), $c = 10.672$ (5) Å, $\beta = 100.24$ (6)°, $U = 2135.5$ Å³. Systematic extinctions: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$. Space group $P2_1/n$ ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$). $D_c = 2.22$ Mg m⁻³ for $Z = 4$. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 11.1$ mm⁻¹. 4091 independent reflexions, $I > 3\sigma(I)$. No absorption correction.

* $\sigma(I)$ is the standard deviation based on simple counting statistics.

Preliminary scans showed the crystal to be quite badly split, but, as no other sample was available, it was decided to collect data in the hope that at least the gross structural features could be determined. The intensities of each independent reflexion with $\sin \theta/\lambda < 0.66 \text{ \AA}^{-1}$ were measured with an ω/θ scan, a variable scan rate and an ω scan angle of $1.00 + 0.35 \tan \theta^\circ$. The preliminary account (Green, Berry, Couldwell & Prout, 1977) used a limited data set ($\sin \theta/\lambda < 0.59 \text{ \AA}^{-1}$; 3057 independent structure amplitudes).

(c) Compound (III): C₂₄H₃₀SiW₂, $M_r = 714.3$, monoclinic, $a = 16.530(2)$, $b = 7.759(1)$, $c = 18.208(2) \text{ \AA}$, $\beta = 110.55(1)^\circ$, $U = 2186.7 \text{ \AA}^3$. Systematic extinctions: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Space group $P2_1/c$. $D_c = 2.17 \text{ Mg m}^{-3}$ for $Z = 4$. Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 10.8 \text{ mm}^{-1}$. 2484 independent reflexions, $I > 3\sigma(I)$.

The intensities of at least two equivalents of every independent reflexion with $\sin \theta/\lambda < 0.59 \text{ \AA}^{-1}$ were measured with an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $1.00 + 0.35 \tan \theta^\circ$. The data were corrected for absorption (North, Phillips & Mathews, 1968). Before absorption corrections were applied the merging R was 0.095 and R_w 0.031; after these corrections R was 0.051 and R_w 0.003.

Structure solution and refinement

The structures were solved by Patterson and Fourier techniques and refined by full-matrix (I) or large block diagonal least squares [(II): block 1: scale and dummy overall isotropic temperature factor (Rollett, 1965), block 2: positional parameters, block 3: corresponding temperature factors; (III): block 1: scale, dummy overall isotropic temperature factor, overall isotropic extinction parameter (Larson, 1967), block 2: positional parameters, block 3: corresponding temperature factors]. The weighting scheme was $w = 1/\sum_{r=1}^n A_r T_r^*(X)$, where n is the number of coefficients, A_r , for a Chebyshev series, T_r^* is the polynomial function, and X is $|F_o|/|F_o(\max)|$ (Rollett, 1965). All non-hydrogen atoms had anisotropic temperature factors.

(a) Compound (I). Difference syntheses permitted the location of the cyclopentadienyl ring H atoms in their expected positions. They were positioned geometrically ($C-H = 1.0 \text{ \AA}$; $U_{\text{iso}} = 0.05 \text{ \AA}^2$) and included in the structure factor calculations, their location being readjusted after each cycle. For the weighting scheme, three coefficients, A_r , were used with values of 12.0, 16.2 and 4.9, respectively, and the final R_w was 0.079 for 1937 reflexions.

(b) Compound (II). H atoms were not located. For the weighting scheme, five coefficients, A_r , were used with values of 11.7, 11.5, -4.3, -7.8 and -2.7,

respectively, and the final R_w was 0.132 for 4091 reflexions.

(c) Compound (III). Difference syntheses showed some evidence for cyclopentadienyl ring and methyl H atoms at their expected positions. However, they were positioned geometrically ($C-H = 1.0 \text{ \AA}$, $U_{\text{iso}} = 0.05 \text{ \AA}^2$) and included in the structure factor calculations, their location being readjusted after each cycle. In the final stages of refinement, an overall isotropic extinction parameter (26.92) was introduced, as well as the weighting scheme with three coefficients, A_r , with values of 421.1, 574.1 and 219.3 respectively. The final R_w was 0.035 for 2484 reflexions.

All calculations were performed on the Oxford University ICL 1906A computer with the *CRYSTALS* package (Carruthers, 1975). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

The final atomic positional parameters are given in Tables 1, 2 and 3,* and bond lengths and angles, with e.s.d.'s calculated from the variance-covariance matrix, in Tables 4, 5 and 6. Projections of the molecules are shown in Figs. 1, 2 and 3. Details of important molecular planes are given in Table 7.

* Lists of structure factors and anisotropic thermal parameters for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34019 (78 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Compound (I) (C₂₀H₂₀W₂): fractional atomic coordinates, with e.s.d.'s in parentheses

	x	y	z
W(1)	0.14797 (7)	0.13089 (5)	0.20080 (5)
C(1)	-0.079 (2)	-0.152 (2)	0.188 (1)
C(2)	0.025 (2)	-0.146 (1)	0.048 (1)
C(3)	0.271 (2)	-0.108 (2)	0.108 (1)
C(4)	0.317 (2)	-0.094 (2)	0.282 (1)
C(5)	0.105 (2)	-0.117 (2)	0.332 (1)
C(6)	0.443 (2)	0.358 (2)	0.183 (2)
C(7)	0.246 (3)	0.438 (2)	0.164 (2)
C(8)	0.163 (3)	0.422 (2)	0.306 (3)
C(9)	0.296 (3)	0.334 (2)	0.415 (2)
C(10)	0.478 (3)	0.295 (2)	0.342 (2)
H(1)	-0.2475	-0.1755	0.1866
H(3)	0.3894	-0.0939	0.0397
H(4)	0.4729	-0.0724	0.3549
H(5)	0.0845	-0.1107	0.4456
H(6)	0.5394	0.3488	0.1014
H(7)	0.1788	0.4935	0.0661
H(8)	0.0265	0.4687	0.3272
H(9)	0.2697	0.3041	0.5239
H(10)	0.6039	0.2347	0.3912

Table 2. Compound (II) (*cis*-C₂₄H₃₀SiW₂): fractional atomic coordinates, with e.s.d.'s in parentheses

	x	y	z
W(1)	0.2725 (1)	0.08701 (4)	0.20973 (9)
W(2)	-0.0673 (1)	0.18946 (4)	0.21371 (9)
Si(1)	0.161 (1)	-0.0515 (3)	0.3353 (7)
C(1)	0.109 (3)	0.0125 (9)	0.232 (2)
C(2)	0.210 (4)	-0.037 (1)	0.512 (2)
C(3)	0.345 (5)	-0.092 (2)	0.305 (3)
C(4)	-0.013 (5)	-0.102 (1)	0.307 (3)
C(11)	0.386 (3)	0.109 (1)	0.043 (3)
C(12)	0.502 (4)	0.089 (1)	0.145 (3)
C(13)	0.477 (4)	0.027 (1)	0.169 (3)
C(14)	0.341 (3)	0.013 (1)	0.076 (3)
C(15)	0.277 (3)	0.059 (1)	-0.001 (3)
C(21)	0.347 (3)	0.096 (1)	0.425 (3)
C(22)	0.185 (3)	0.107 (1)	0.397 (2)
C(23)	0.149 (3)	0.1569 (9)	0.315 (2)
C(24)	0.311 (3)	0.175 (1)	0.294 (2)
C(25)	0.428 (3)	0.140 (1)	0.363 (3)
C(31)	-0.177 (3)	0.226 (1)	0.384 (3)
C(32)	-0.028 (4)	0.244 (1)	0.404 (3)
C(33)	-0.001 (4)	0.278 (1)	0.292 (4)
C(34)	-0.157 (3)	0.279 (1)	0.204 (3)
C(35)	-0.267 (5)	0.244 (1)	0.268 (3)
C(41)	-0.104 (3)	0.199 (1)	0.003 (3)
C(42)	-0.204 (4)	0.154 (1)	0.028 (2)
C(43)	-0.102 (2)	0.1067 (7)	0.088 (2)
C(44)	0.063 (3)	0.124 (1)	0.101 (2)
C(45)	0.053 (4)	0.183 (1)	0.048 (2)

Table 3. Compound (III) (*trans*-C₂₄H₃₀SiW₂): fractional atomic coordinates, with e.s.d.'s in parentheses

	x	y	z
W(1)	0.17290 (2)	0.09300 (5)	0.22205 (2)
W(2)	0.38441 (2)	0.32755 (5)	0.34046 (2)
Si(1)	0.1947 (2)	-0.1412 (5)	0.0523 (2)
C(1)	0.2399 (6)	-0.072 (1)	0.1566 (6)
C(2)	0.192 (1)	0.041 (2)	-0.0152 (8)
C(3)	0.265 (1)	-0.313 (2)	0.0336 (8)
C(4)	0.0846 (9)	-0.236 (2)	0.0171 (7)
C(11)	0.1146 (8)	0.009 (2)	0.3116 (8)
C(12)	0.0454 (7)	0.051 (2)	0.2394 (8)
C(13)	0.0457 (7)	-0.069 (2)	0.1793 (8)
C(14)	0.1121 (8)	-0.188 (1)	0.2152 (7)
C(15)	0.1548 (8)	-0.141 (2)	0.2969 (7)
C(21)	0.1437 (7)	0.297 (1)	0.1257 (7)
C(22)	0.2359 (7)	0.299 (1)	0.1684 (6)
C(23)	0.2593 (6)	0.350 (1)	0.2471 (6)
C(24)	0.1776 (7)	0.376 (1)	0.2575 (7)
C(25)	0.1081 (7)	0.347 (1)	0.1836 (7)
C(31)	0.5026 (8)	0.504 (2)	0.3918 (7)
C(32)	0.5136 (7)	0.391 (2)	0.3329 (7)
C(33)	0.4503 (8)	0.429 (2)	0.2583 (8)
C(34)	0.4020 (9)	0.570 (2)	0.271 (1)
C(35)	0.434 (1)	0.613 (2)	0.353 (1)
C(41)	0.4482 (8)	0.078 (1)	0.3874 (6)
C(42)	0.4075 (8)	0.140 (2)	0.4393 (6)
C(43)	0.3173 (8)	0.135 (1)	0.3958 (6)
C(44)	0.2986 (6)	0.075 (1)	0.3159 (6)
C(45)	0.3836 (7)	0.041 (1)	0.3130 (7)
H(111)	0.2940	-0.0079	0.1613
H(112)	0.2553	-0.1817	0.1873
H(221)	0.1679	-0.0003	-0.0707
H(222)	0.2526	0.0841	-0.0041
H(223)	0.1558	0.1359	-0.0070
H(331)	0.2404	-0.3501	-0.0225
H(332)	0.3246	-0.2670	0.0451
H(333)	0.2673	-0.4146	0.0683
H(441)	0.0680	-0.2673	-0.0393
H(442)	0.0840	-0.3412	0.0486
H(443)	0.0426	-0.1495	0.0237
H(11)	0.1311	0.0742	0.3624
H(12)	0.0036	0.1480	0.2323
H(13)	0.0064	-0.0690	0.1230
H(14)	0.1275	-0.2891	0.1887
H(15)	0.2042	-0.2043	0.3360
H(21)	0.1124	0.2676	0.0693
H(22)	0.2793	0.2660	0.1438
H(24)	0.1701	0.4080	0.3081
H(25)	0.0449	0.3598	0.1742
H(31)	0.5374	0.5043	0.4493
H(32)	0.5592	0.3001	0.3430
H(33)	0.4415	0.3679	0.2074
H(34)	0.3533	0.6299	0.2290
H(35)	0.4112	0.7064	0.3779
H(41)	0.5119	0.0623	0.4013
H(42)	0.4362	0.1782	0.4950
H(43)	0.2718	0.1703	0.4175
H(45)	0.3953	-0.0009	0.2657

The unit cell for each compound contains (I) one, (II) four and (III) four molecules with the structures shown in Figs. 1, 2 and 3 respectively. The dimer in (I) has crystallographic point symmetry C_i in space group $P\bar{1}$. The successful refinement was taken as confirmation of this space group and no calculations were made in $P1$.

The bis[bis(η^5 -cyclopentadienyl)tungsten] skeleton has the *trans* configuration in (I), *cis* in (II) and *trans* in (III). Figs. 1 and 3 show the similarity between the skeletons in (I) and (III), that is, the two with *trans* configurations. The W atoms, separated by (I)

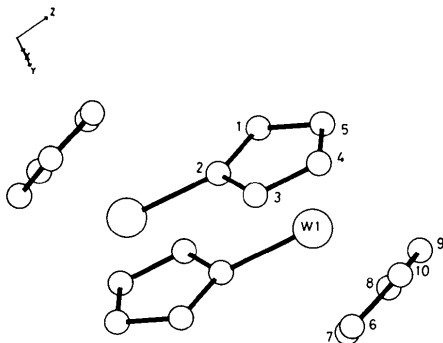


Fig. 1. Projection of $trans\text{-}\{(\eta^5\text{-C}_5\text{H}_5)(\text{H})\text{W}\}[\mu\text{-}(\sigma\text{-}\eta^5\text{-C}_5\text{H}_5)]_2\text{-W}(\text{H})(\eta^5\text{-C}_5\text{H}_5)$ on to the plane containing the two W atoms and the normals to the $(\eta^5\text{-C}_5\text{H}_5)$ rings. For clarity, the C atoms are labelled by their serial number only.

3.811 (1), (II) 3.816 (1) and (III) 3.859 (1) Å, are bridged by C atoms provided by the adjacent η^5 -cyclopentadienyl rings, which are therefore formulated as C_5H_4 . The coordination sphere about each W atom is completed either by a $\text{CH}_2\text{Si}(\text{CH}_3)_3$ group [W(1) in (II) and (III)] or by a hydrido ligand [(I), and W(2) in (II)

Table 4. Compound (I) (C₂₀H₂₀W₂): interatomic distances (Å) and bond angles (°)

W(1)–W(1')	3.811 (1)	W(1)–C(2')	2.19 (1)
W(1)–C(1)	2.32 (1)	W(1)–C(6)	2.28 (1)
W(1)–C(2)	2.35 (1)	W(1)–C(7)	2.37 (1)
W(1)–C(3)	2.27 (1)	W(1)–C(8)	2.35 (1)
W(1)–C(4)	2.24 (1)	W(1)–C(9)	2.27 (1)
W(1)–C(5)	2.25 (1)	W(1)–C(10)	2.23 (1)
C(1)–C(2)	1.45 (2)	C(6)–C(7)	1.42 (2)
C(2)–C(3)	1.45 (2)	C(7)–C(8)	1.40 (3)
C(3)–C(4)	1.45 (2)	C(8)–C(9)	1.39 (3)
C(4)–C(5)	1.41 (2)	C(9)–C(10)	1.44 (2)
C(5)–C(1)	1.46 (2)	C(10)–C(6)	1.44 (2)
C(2')–W(1)–Q(1)*	101	C(2')–W(1)–Q(2)	108
Q(1)–W(1)–Q(2)	147		
C(5)–C(1)–C(2)	108 (1)	C(10)–C(6)–C(7)	108 (1)
C(1)–C(2)–C(3)	107 (1)	C(6)–C(7)–C(8)	107 (1)
C(2)–C(3)–C(4)	109 (1)	C(7)–C(8)–C(9)	111 (1)
C(3)–C(4)–C(5)	108 (1)	C(8)–C(9)–C(10)	108 (1)
C(4)–C(5)–C(1)	108 (1)	C(9)–C(10)–C(6)	107 (1)

Symmetry code: superscript: none *x, y, z*, (i) $\bar{x}, \bar{y}, \bar{z}$.

* Q represents the centroid of the appropriate plane: Q(1) ring C(1) to C(5); Q(2) ring C(6) to C(10).

and (III)]. The hydrido H atom is postulated because, although there is no direct evidence for it from the electron density distribution, its presence is inferred from NMR measurements and the observed stereochemical arrangement about the W atom, and it is required to bring the W atom to the 18 e configuration.

The bis(η^5 -cyclopentadienyl)tungsten groupings in the molecules have significantly different geometries from those observed in many other systems. For (I) the W–ring perpendicular distances are 1.93 and 1.95 Å, and the angle between the ring normals is 141°. In (II) these distances are in the range 1.91–1.95 Å and the angles between the ring normals are 137° for W(1) and 142° for W(2); in (III) the distances range from 1.93 to 1.97 Å, and the angles are 136° W(1) and 141° W(2).

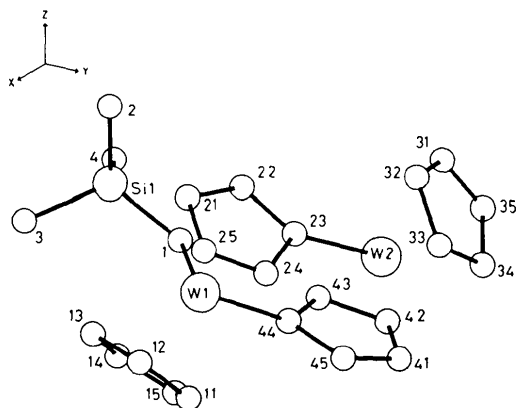


Fig. 2. Projection of *cis*-(η^5 -C₅H₅)₂[CH₂Si(CH₃)₃]W(μ - σ : η^5 -C₅H₄)₂W(H)(η^5 -C₅H₅) onto the plane containing the two W atoms and the normals to the (η^5 -C₅H₅) rings. For clarity, the C atoms are labelled by their serial number only.

Table 5. Compound (II) (*cis*-C₂₄H₃₀SiW₂): interatomic distances (Å) and bond angles (°)

W(1)–W(2)	3.816 (1)	Si(1)–C(1)	1.86 (2)
W(1)–C(1)	2.29 (2)	Si(1)–C(2)	1.89 (3)
W(1)–C(44)	2.17 (3)	Si(1)–C(3)	1.94 (4)
W(1)–C(11)	2.25 (2)	Si(1)–C(4)	1.90 (4)
W(1)–C(12)	2.24 (3)	C(11)–C(12)	1.43 (5)
W(1)–C(13)	2.37 (3)	C(12)–C(13)	1.48 (4)
W(1)–C(14)	2.39 (3)	C(13)–C(14)	1.45 (5)
W(1)–C(15)	2.35 (2)	C(14)–C(15)	1.40 (4)
W(1)–C(21)	2.28 (3)	C(15)–C(11)	1.53 (5)
W(1)–C(22)	2.32 (2)	C(21)–C(22)	1.42 (4)
W(1)–C(23)	2.34 (2)	C(22)–C(23)	1.45 (3)
W(1)–C(24)	2.23 (2)	C(23)–C(24)	1.53 (3)
W(1)–C(25)	2.29 (3)	C(24)–C(25)	1.40 (4)
W(2)–C(23)	2.15 (2)	C(25)–C(21)	1.47 (4)
W(2)–C(31)	2.36 (2)	C(31)–C(32)	1.35 (4)
W(2)–C(32)	2.36 (3)	C(32)–C(33)	1.48 (5)
W(2)–C(33)	2.26 (2)	C(33)–C(34)	1.52 (4)
W(2)–C(34)	2.21 (3)	C(34)–C(35)	1.50 (5)
W(2)–C(35)	2.32 (3)	C(35)–C(31)	1.41 (5)
W(2)–C(41)	2.23 (3)	C(41)–C(42)	1.42 (4)
W(2)–C(42)	2.28 (3)	C(42)–C(43)	1.49 (3)
W(2)–C(43)	2.33 (2)	C(43)–C(44)	1.48 (3)
W(2)–C(44)	2.36 (2)	C(44)–C(45)	1.49 (3)
W(2)–C(45)	2.22 (3)	C(45)–C(41)	1.42 (4)

C(1)–W(1)–C(44)	82.5 (9)	C(23)–W(2)–Q(5)	107
C(1)–W(1)–Q(3)*	105	C(23)–W(2)–Q(6)	97
C(1)–W(1)–Q(4)	107	Q(5)–W(2)–Q(6)	150
C(44)–W(1)–Q(3)	107	C(1)–Si(1)–C(2)	116 (1)
C(44)–W(1)–Q(4)	97	C(1)–Si(1)–C(3)	115 (1)
Q(3)–W(1)–Q(4)	142	C(1)–Si(1)–C(4)	107 (1)
W(1)–C(1)–Si(1)	125 (1)	C(2)–Si(1)–C(3)	102 (1)
		C(2)–Si(1)–C(4)	107 (2)
		C(3)–Si(1)–C(4)	110 (2)
C(15)–C(11)–C(12)	107 (3)	C(35)–C(31)–C(32)	115 (3)
C(11)–C(12)–C(13)	110 (3)	C(31)–C(32)–C(33)	109 (3)
C(12)–C(13)–C(14)	104 (3)	C(32)–C(33)–C(34)	104 (3)
C(13)–C(14)–C(15)	115 (3)	C(33)–C(34)–C(35)	107 (3)
C(14)–C(15)–C(11)	104 (3)	C(34)–C(35)–C(31)	104 (3)
C(25)–C(21)–C(22)	108 (2)	C(45)–C(41)–C(42)	110 (2)
C(21)–C(22)–C(23)	112 (2)	C(41)–C(42)–C(43)	106 (3)
C(22)–C(23)–C(24)	101 (2)	C(42)–C(43)–C(44)	110 (2)
C(23)–C(24)–C(25)	112 (2)	C(43)–C(44)–C(45)	103 (2)
C(24)–C(25)–C(21)	106 (2)	C(44)–C(45)–C(41)	111 (2)

* Q represents the centroid of the appropriate plane: Q(3) ring C(11) to C(15); Q(4) ring C(21) to C(25); Q(5) ring C(31) to C(35); Q(6) ring C(41) to C(45).

Typical values in simple bis(η^5 -cyclopentadienyl)tungsten systems are 1.99 Å and 134° in (η^5 -C₅H₅)₂-W(CH₂C₆H₅(CH₃)₂)₂ (Forder, Jefferson & Prout, 1975), 1.99 Å and 134° in [(η^5 -C₅H₅)₂W(CH₃)CH₂-CH₂P(CH₃)₂C₆H₅]⁺ (Forder, Gale & Prout, 1975), and 1.99 Å and 132.4° in (η^5 -C₅H₅)₂W(μ -SC₆H₅)₂-W(CO)₄ (Prout & Rees, 1974). The correlation between short metal–ring distances and wide inter-ring angles could be a result of the geometrical requirements of σ bonding to the adjacent W atom, but it is probably steric in origin, resulting from the need to restrict non-bonded interactions between cyclopentadienyl ring H atoms, as it occurs in other systems where there are no bridging cyclopentadienyl groups; for

Table 6. Compound (III) (*trans*-C₂₄H₃₀SiW₂): interatomic distances (Å) and bond angles (°)

W(1)–W(2)	3.859 (1)	Si(1)–C(1)	1.86 (1)
W(1)–C(1)	2.284 (9)	Si(1)–C(2)	1.86 (2)
W(1)–C(44)	2.18 (1)	Si(1)–C(3)	1.88 (2)
W(1)–C(11)	2.26 (1)	Si(1)–C(4)	1.86 (1)
W(1)–C(12)	2.26 (1)	C(11)–C(12)	1.44 (2)
W(1)–C(13)	2.34 (1)	C(12)–C(13)	1.44 (2)
W(1)–C(14)	2.39 (1)	C(13)–C(14)	1.41 (2)
W(1)–C(15)	2.35 (1)	C(14)–C(15)	1.45 (2)
W(1)–C(21)	2.28 (1)	C(15)–C(11)	1.42 (2)
W(1)–C(22)	2.30 (1)	C(21)–C(22)	1.45 (2)
W(1)–C(23)	2.40 (1)	C(22)–C(23)	1.41 (2)
W(1)–C(24)	2.28 (1)	C(23)–C(24)	1.44 (1)
W(1)–C(25)	2.23 (1)	C(24)–C(25)	1.45 (2)
W(2)–C(23)	2.18 (1)	C(25)–C(21)	1.43 (2)
W(2)–C(31)	2.30 (1)	C(31)–C(32)	1.45 (2)
W(2)–C(32)	2.24 (1)	C(32)–C(33)	1.43 (2)
W(2)–C(33)	2.28 (1)	C(33)–C(34)	1.42 (2)
W(2)–C(34)	2.35 (1)	C(34)–C(35)	1.44 (2)
W(2)–C(35)	2.35 (1)	C(35)–C(31)	1.39 (2)
W(2)–C(41)	2.23 (1)	C(41)–C(42)	1.42 (2)
W(2)–C(42)	2.24 (1)	C(42)–C(43)	1.42 (2)
W(2)–C(43)	2.29 (1)	C(43)–C(44)	1.46 (2)
W(2)–C(44)	2.37 (1)	C(44)–C(45)	1.45 (1)
W(2)–C(45)	2.28 (1)	C(45)–C(41)	1.43 (2)
C(1)–W(1)–C(44)	82.5 (4)	C(23)–W(2)–Q(9)	107
C(1)–W(1)–Q(7)*	105	C(23)–W(2)–Q(10)	97
C(1)–W(1)–Q(8)	108	Q(9)–W(2)–Q(10)	147
C(44)–W(1)–Q(7)	107	C(1)–Si(1)–C(2)	111.3 (7)
C(44)–W(1)–Q(8)	96	C(1)–Si(1)–C(3)	109.8 (5)
Q(7)–W(1)–Q(8)	142	C(1)–Si(1)–C(4)	117.5 (5)
W(1)–C(1)–Si(1)	126.9 (5)	C(2)–Si(1)–C(3)	106.9 (8)
		C(2)–Si(1)–C(4)	106.3 (8)
		C(3)–Si(1)–C(4)	104.5 (7)
C(15)–C(11)–C(12)	107 (1)	C(35)–C(31)–C(32)	106 (1)
C(11)–C(12)–C(13)	110 (1)	C(31)–C(32)–C(33)	110 (1)
C(12)–C(13)–C(14)	106 (1)	C(32)–C(33)–C(34)	106 (1)
C(13)–C(14)–C(15)	110 (1)	C(33)–C(34)–C(35)	109 (1)
C(14)–C(15)–C(11)	108 (1)	C(34)–C(35)–C(31)	109 (1)
C(25)–C(21)–C(22)	103 (1)	C(45)–C(41)–C(42)	109 (1)
C(21)–C(22)–C(23)	114 (1)	C(41)–C(42)–C(43)	106 (1)
C(22)–C(23)–C(24)	104 (1)	C(42)–C(43)–C(44)	112 (1)
C(23)–C(24)–C(25)	109 (1)	C(43)–C(44)–C(45)	103 (1)
C(24)–C(25)–C(21)	109 (1)	C(44)–C(45)–C(41)	110 (1)

* Q represents the centroid of the appropriate plane: Q(7) ring C(11) to C(15); Q(8) ring C(21) to C(25); Q(9) ring C(31) to C(35); Q(10) ring C(41) to C(45).

example, 1.90–1.93 Å and 148–149° in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{-M(H)Li}]_4$ ($M = \text{Mo, W}$) (Forder & Prout, 1974b), 1.94–1.95 Å and 143–145° in $[\text{Mo(H)(C}_5\text{H}_5\text{)}\text{-}(\text{C}_5\text{H}_4)_2\text{Al}_3(\text{CH}_3)_5]$, and 1.93–1.94 Å and 151° in $[\text{Mo(C}_5\text{H}_4)_2\text{Al}_2(\text{CH}_3)_3]$ (Forder & Prout, 1974a). Also, in support of this steric argument, for (II) and (III) the inter-ring angles are smaller at W(1) with the more bulky CH₂Si(CH₃)₃ ligand.

The W–ring perpendicular distances are shorter for those rings involved in the σ bonding; that is, ring C(1) to C(5) in (I), and rings C(21) to C(25) and C(41) to C(45) in (II) and (III). The constraint imposed by the bridging C₅H₄ groups by the bonding to the adjacent W atom is important, as it also leads to short W–C σ

Table 7. Equations of least-squares best planes and, in square brackets, distances (Å) of atoms from the planes

The equations are referred to the crystal axes and x , y , and z are fractional coordinates.

Compound (I)

Plane (1): ring C(1) to C(5)

$$1.026x - 7.677y + 0.449z = 1.165$$

[C(1) 0.004, C(2) 0.003, C(3) –0.008, C(4) 0.011, C(5) –0.009, W(1)* –1.928]

Normal to W(1) meets plane 0.11 Å from centroid.

Plane (2): ring C(6) to C(10)

$$-2.173x - 5.904y - 1.960z = -3.440$$

[C(6) 0.003, C(7) 0.003, C(8) –0.008, C(9) 0.010, C(10) –0.008, W(1)* 1.952]

Normal to W(1) meets plane 0.15 Å from centroid.

Compound (II)

Plane (3): ring C(11) to C(15)

$$-6.188x + 5.769y + 8.298z = -1.397$$

[C(11) –0.011, C(12) 0.006, C(13) 0.003, C(14) –0.011, C(15) 0.013, W(1)* 1.953]

Normal to W(1) meets plane 0.17 Å from centroid.

Plane (4): ring C(21) to C(25)

$$0.588x - 13.817y - 8.539z = -4.761$$

[C(21) 0.016, C(22) –0.006, C(23) –0.006, C(24) 0.016, C(25) –0.020, W(1)* 1.928]

Normal to W(1) meets plane 0.07 Å from centroid.

Plane (5): ring C(31) to C(35)

$$-2.923x + 19.328y + 5.282z = 6.921$$

[C(31) 0.000, C(32) 0.001, C(33) –0.001, C(34) 0.001, C(35) –0.001, W(2)* –1.934]

Normal to W(2) meets plane 0.20 Å from centroid.

Plane (6): ring C(41) to C(45)

$$1.748x - 8.897y - 9.850z = -1.995$$

[C(41) 0.013, C(42) –0.008, C(43) 0.000, C(44) 0.007, C(45) –0.013, W(2)* –1.914]

Normal to W(2) meets plane 0.11 Å from centroid.

Compound (III)

Plane (7): ring C(11) to C(15)

$$-12.828x - 4.473y + 9.321z = 1.407$$

[C(11) –0.014, C(12) 0.016, C(13) –0.011, C(14) 0.003, C(15) 0.007, W(1)* –1.971]

Normal to W(1) meets plane 0.14 Å from centroid.

Plane (8): ring C(21) to C(25)

$$2.032x + 7.444y - 5.118z = 1.854$$

[C(21) 0.004, C(22) –0.013, C(23) 0.017, C(24) –0.015, C(25) 0.007, W(1)* –1.947]

Normal to W(1) meets plane 0.14 Å from centroid.

Plane (9): ring C(31) to C(35)

$$-12.291x - 5.023y + 7.606z = -5.736$$

[C(31) 0.004, C(32) –0.010, C(33) 0.012, C(34) –0.010, C(35) 0.003, W(2)* 1.955]

Normal to W(2) meets plane 0.11 Å from centroid.

Plane (10): ring C(41) to C(45)

$$2.762x + 7.286y - 6.188z = -0.583$$

[C(41) –0.009, C(42) 0.007, C(43) –0.003, C(44) –0.003, C(45) 0.007, W(2)* 1.925]

Normal to W(2) meets plane 0.11 Å from centroid.

* Atoms not included in the plane calculations.

bonds: (I) W(1)—C(2¹) 2.19 (1), (II) W(1)—C(44) 2.17 (3), W(2)—C(23) 2.15 (2) and (III) W(1)—C(44) 2.18 (1), W(2)—C(23) 2.18 (1) Å. A similar situation occurs in [Mo(C₅H₄)₂Al₂(CH₃)₃]₂ where the constraint imposed on the bridging C₅H₄ groups by bonding to the Mo leads to a short Al—C bond (Forder & Prout, 1974a).

In simple (η^5 -C₅H₅)MX₂ systems the projection of the metal atom on to the best plane of a cyclopentadienyl ring typically lies within about 0.1 Å of the ring centroid (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). It might be expected that one of the effects of the W—C₅H₄ σ bonding would be to pull the ring away from this idealized position; however, this is not so and these distances are quite normal at 0.07–0.20 Å (Table 7).

In the η^5 -cyclopentadienyl rings the C—C bonds vary from (I) 1.39 (3) to 1.46 (2) [mean 1.43 (2)], (II) 1.35 (4) to 1.53 (5) [mean 1.46 (5)] and (III) 1.39 (2) to 1.46 (2) Å [mean 1.43 (2) Å], similar to those found in other complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The C—C—C angles vary from 107 (1)–111 (1) [mean 108 (1)] (I), 101 (2)–115 (3) [mean 108 (4)] (II), and 103 (1)–114 (1)° [mean 108 (3)°] (III). The W—C(ring) distances are in the range 2.23 (1)–2.37 (1) [mean 2.29 (5)] (I), 2.21–2.39 (3) [mean 2.30 (6)] (II) and 2.23 (1)–2.40 (1) Å [mean 2.30 (3) Å] (III). Although the C—C bonds show no systematic variation, it is noticeable that in each of the C₅H₄ groups the longest W—C distance and the smallest C—C—C angle are associated with the σ -bonding C atom. However, as in other C₅H₄ systems (Forder & Prout, 1974a), the present data offer no real evidence for any significant loss of π character from

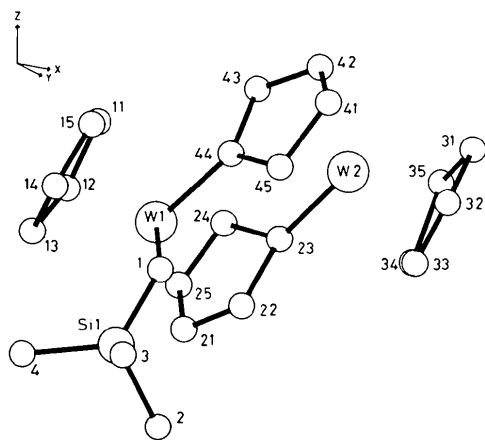


Fig. 3. Projection of *trans*-{(η^5 -C₅H₅)[CH₂Si(CH₃)₃]W[μ -(σ : η^5 -C₅H₄)₂W(H)(η^5 -C₅H₅)]} on to the plane containing the two W atoms and the normals to the (η^5 -C₅H₅) rings. For clarity, the C atoms are labelled by their serial number only.

these rings. The results for least-squares planes through the η^5 -cyclopentadienyl rings are given in Table 7, and the individual rings are planar within experimental error.

For (II) and (III) containing the CH₂Si(CH₃)₃ group, the W(1)—C(1) σ -bond lengths of 2.29 (2) and 2.284 (9) Å, respectively, are longer than those found in other systems; for example, 2.05 (3)–2.13 (3) in W₂[CSi(CH₃)₃]₂[CH₂Si(CH₃)₃]₄ (Chisholm, Cotton, Extine & Murillo, 1978) and 2.03 (4)–2.23 (3) Å in W₂[CH₂Si(CH₃)₃]₆ (Chisholm, Cotton, Extine & Stults, 1976). However, they are similar to the W—C σ -bond lengths of 2.276 (7) and 2.291 (7) Å found in (η^5 -C₅H₅)₂W[CH₂C₆H₃(CH₃)₂]₂ (Forder, Jefferson & Prout, 1975). The Si—C lengths are in the ranges 1.86 (2)–1.94 (4) (II) and 1.86 (2)–1.88 (2) Å (III), and the angles vary from 102 (1)–116 (1) (II) and 104.5 (7)–117.5 (5)° (III). These agree well with Si—C lengths of 1.75 (5)–1.99 (8) and 1.80 (5)–2.04 (4) Å, and C—Si—C bond angles of 106 (2)–114 (2) and 104 (2)–118 (2)° in W₂[CSi(CH₃)₃]₂[CH₂Si(CH₃)₃]₄ and W₂[CH₂Si(CH₃)₃]₆ respectively.

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