Nature of the Novel $C_{15}H_{15}$ Ligand in $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_{15}H_{15})]$ †

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A structural study of the compound originally formulated as $[W(CO)_2(C_5H_5)_4]$ has revealed that it is actually $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_{15}H_{15})]$. The substance crystallizes in the monoclinic space group $P2_1/c$ with a = 13.578(8), b = 20.967(9), c = 13.831(8) Å, β = 109.72(6)°, and Z = 8 for D_c = 1.79 g cm^{-3}. The final R value was 0.079 for 2 458 independent observed reflections. In the two crystallographically independent molecules the W–C(η^3) bonds show significant internal variation: the unique W–C lengths average 2.19 Å and the remaining ones, 2.36 Å. The W–C(η^5) bond lengths average 2.34 Å. The five-membered ring bonded in an allylic fashion to the tungsten atom contains two tetrahedral carbon atoms, each of which is bonded to one C_5H_5 group and one hydrogen atom. The two C_5H_5 sub-units may be viewed as dienes and differ in the location of the tetrahedral carbon atoms. It exists in the 2 position on one and the 3 position on the other. The C_5H_5 groups are in a *cis*-arrangement, *exo* to the tungsten atom.

THE cyclopentadienyl group has well known ability to exist as either an η^5 or a σ ligand. Rarely, an intermediate co-ordination ability may be exhibited because of electronic or steric effects. The complexes $[Mo(NO)(C_5H_5)_3]$ [1] and $[W(CO)_2(C_5H_5)_2]$ [2] are examples of the former, and $[TaCl_2(C_5H_5)(C_2H_4)(PMe_2Ph)]$,[3] the latter. Because of the fluxional nature of the σ-C_5H_5 moiety in solution the differentiation of the two extreme possibilities *via* n.m.r. spectroscopy may not be possible.[4] From electronic considerations, $[W(CO)_2(C_5H_5)_4]$ [5] was initially formulated as $[W(CO)_2(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)_3]$. This was reasonable since the compound was prepared by the reaction of $Na[C_5H_5]$ with $[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$, but the n.m.r. spectrum was difficult to interpret. One ring was definitely π bonded, but the remaining three C_5H_5 ligands gave rise to a very complicated ^{1}H n.m.r. spectrum. An increase in temperature failed to simplify the situation. In order to clarify the nature of the bonding in $[W(CO)_2(C_5H_5)_4]$ an *X*-ray crystallographic study was undertaken. A preliminary report [6] on the compound showed the existence of a new $C_{15}H_{15}$ ligand. Since interest appears high in the chemistry of this novel group,[7] we thought it important to describe the structure in detail.

EXPERIMENTAL

X-Ray Data Collection, Structure Determination and Refinement for $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_{15}H_{15})]$.—*Crystal data.* $C_{22}H_{20}O_2W$, $M = 500.2$, Monoclinic, $a = 13.578(8)$, $b = 20.967(9)$, $c = 13.831(8)$ Å, $\beta = 109.72(6)°$, $U = 3\,706.6$, $Z = 8$, $D_c = 1.79$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 65.9$ cm^{-1}, space group $P2_1/c$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta \geqslant 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of approximate dimensions 0.42 × 0.34 × 0.40 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were measured by the ω—2θ scan technique in a manner similar to that described previously.[8] All reflections in one independent quadrant out to $2\theta \leqslant 50°$ were measured; 2 458 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption. (The crystal was of rather regular shape, but the faces were difficult to measure because it was coated with silicone grease.)

Full-matrix, least-squares refinement was carried out using the Busing and Levy ORFLS program.‡ The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for W, O, and C were taken from Cromer and Waber,[9] those for H were from ref. 10. The scattering for tungsten was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[11]

The positions of the tungsten atoms were deduced by the inspection of a Patterson map, and the subsequent calculation of Fourier maps afforded the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.101$. Conversion of the two independent tungsten atoms to anisotropic thermal parameters and further refinement led to $R = 0.081$. The hydrogen atoms of the η^5-C_5H_5 rings were placed in calculated positions and their parameters were not refined. Additional cycles of refinement of the non-hydrogen atoms led to final values of $R = 0.079$ and $R' = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{\frac{1}{2}} = 0.086$. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviations. The standard deviation of an observation of unit weight was 9.14. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ *vs* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 1. The thermal parameters, least-squares plane results, and the observed and calculated structure factor amplitudes are given in Supplementary Publication No. SUP 22742 (21 pp.).§

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† Dicarbonyl(η-cyclopentadienyl)[1–3-η-(4-cyclopenta-1′,3′-dienyl)-5-(cyclopenta-1″,4″-dienyl)cyclopentenyl]tungsten.

‡ Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distances and angles with estimated standard deviations by W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), BPL (least-squares planes, by W. E. Hunter), and FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program).

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

DISCUSSION

The molecular structure and atom-numbering scheme for the two crystallographically independent molecules are shown in Figure 1. The two are structurally equivalent within the accuracy of the determination. The central ring of both η^3-$C_{15}H_{15}$ ligands contains two tetrahedral carbon atoms, each of which is bonded to one C_5H_5 group and one hydrogen atom. The C_5H_5 units are in a *cis* arrangement, *exo* to the tungsten atom.

TABLE 1

Final fractional co-ordinates for [$W(CO)_2(\eta^5$-$C_5H_5)(\eta^3$-$C_{15}H_{15})$] with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
W(1)	0.405 4(1)	0.237 38(6)	0.104 6(1)
W(2)	−0.085 9(1)	0.315 42(8)	0.287 8(1)
O(1)	0.295(2)	0.198(1)	−0.117(2)
O(2)	0.571(2)	0.289(1)	0.029(2)
O(3)	0.066(2)	0.318(1)	0.512(2)
O(4)	−0.201(3)	0.208(2)	0.358(3)
C(1)	0.336(2)	0.212(1)	−0.033(2)
C(2)	0.492(3)	0.258(2)	0.049(3)
C(3)	0.433(3)	0.203(2)	0.280(3)
C(4)	0.523(3)	0.196(2)	0.254(3)
C(5)	0.506(3)	0.153(2)	0.175(3)
C(6)	0.414(4)	0.133(2)	0.173(3)
C(7)	0.352(4)	0.176(3)	0.219(4)
C(8)	0.359(3)	0.377(2)	0.007(2)
C(9)	0.406(3)	0.352(2)	0.120(3)
C(10)	0.313(3)	0.316(2)	0.132(3)
C(11)	0.251(3)	0.296(2)	0.037(2)
C(12)	0.256(3)	0.340(2)	−0.049(2)
C(13)	0.157(3)	0.380(2)	−0.092(3)
C(14)	0.077(4)	0.383(2)	−0.055(4)
C(15)	−0.006(4)	0.435(3)	−0.134(4)
C(16)	0.041(4)	0.449(2)	−0.209(4)
C(17)	0.133(4)	0.421(2)	−0.190(3)
C(18)	0.337(3)	0.453(2)	0.021(3)
C(19)	0.373(4)	0.501(2)	−0.034(4)
C(20)	0.338(4)	0.559(2)	0.021(4)
C(21)	0.283(4)	0.543(3)	0.086(4)
C(22)	0.282(4)	0.472(2)	0.090(3)
C(23)	0.009(3)	0.316(2)	0.417(3)
C(24)	−0.149(5)	0.252(3)	0.346(4)
C(25)	0.033(4)	0.330(3)	0.205(4)
C(26)	−0.048(4)	0.349(2)	0.143(4)
C(27)	−0.111(4)	0.296(3)	0.115(4)
C(28)	−0.054(5)	0.252(3)	0.169(4)
C(29)	0.037(5)	0.278(3)	0.225(5)
C(30)	−0.161(2)	0.388(2)	0.454(2)
C(31)	−0.106(2)	0.409(2)	0.376(2)
C(32)	−0.186(3)	0.398(2)	0.264(2)
C(33)	−0.249(3)	0.352(2)	0.283(2)
C(34)	−0.263(3)	0.352(2)	0.386(2)
C(35)	−0.361(3)	0.390(2)	0.376(3)
C(36)	−0.435(4)	0.372(2)	0.422(3)
C(37)	−0.525(3)	0.421(2)	0.389(3)
C(38)	−0.488(3)	0.468(2)	0.334(3)
C(39)	−0.397(3)	0.454(2)	0.318(3)
C(40)	−0.183(3)	0.448(2)	0.510(3)
C(41)	−0.225(4)	0.442(2)	0.597(4)
C(42)	−0.223(4)	0.509(3)	0.634(4)
C(43)	−0.191(4)	0.544(2)	0.574(4)
C(44)	−0.161(3)	0.510(2)	0.495(3)
H(1)]C(3)]	0.456	0.227	0.348
H(2)[C(4)]	0.595	0.219	0.276
H(3)[C(5)]	0.543	0.130	0.138
H(4)[C(6)]	0.349	0.100	0.145
H(5)[C(7)]	0.289	0.202	0.236
H(6)[C(25)]	0.002	0.381	0.218
H(7)[C(26)]	−0.118	0.377	0.075
H(8)[C(27)]	−0.170	0.245	0.098
H(9)[C(28)]	0.008	0.210	0.211
H(10)[C(29)]	0.126	0.318	0.265

TABLE 2

Interatomic distances (Å) and angles (°) for [$W(CO)_2(\eta^5$-$C_5H_5)(\eta^3$-$C_{15}H_{15})$] with estimated standard deviations in parentheses

(*a*) Bond distances

W(1)–C(1)	1.89(3)	W(2)–C(23)	1.82(4)
W(1)–C(2)	1.67(4)	W(2)–C(24)	1.90(6)
W(1)–C(3)	2.43(3)	W(2)–C(25)	2.29(5)
W(1)–C(4)	2.31(4)	W(2)–C(26)	2.34(4)
W(1)–C(5)	2.24(4)	W(2)–C(27)	2.34(6)
W(1)–C(6)	2.38(5)	W(2)–C(28)	2.27(5)
W(1)–C(7)	2.33(5)	W(2)–C(29)	2.27(6)
W(1)–C(8)	2.41(4)	W(2)–C(31)	2.38(3)
W(1)–C(10)	2.18(3)	W(2)–C(32)	2.16(3)
W(1)–C(11)	2.34(3)	W(2)–C(33)	2.32(3)
O(1)–C(1)	1.15(3)	O(3)–C(23)	1.28(4)
O(2)–C(2)	1.36(4)	O(4)–C(24)	1.21(6)
C(3)–C(4)	1.39(5)	C(25)–C(26)	1.21(6)
C(4)–C(5)	1.38(5)	C(26)–C(27)	1.37(6)
C(5)–C(6)	1.31(5)	C(27)–C(28)	1.28(6)
C(6)–C(7)	1.52(6)	C(28)–C(29)	1.33(7)
C(7)–C(3)	1.27(5)	C(29)–C(25)	1.13(7)
C(8)–C(9)	1.58(5)	C(30)–C(31)	1.56(4)
C(9)–C(10)	1.54(5)	C(31)–C(32)	1.58(4)
C(10)–C(11)	1.37(4)	C(32)–C(33)	1.37(4)
C(11)–C(12)	1.53(4)	C(33)–C(34)	1.50(4)
C(12)–C(8)	1.56(4)	C(34)–C(30)	1.58(4)
C(12)–C(13)	1.52(5)	C(34)–C(35)	1.51(5)
C(13)–C(14)	1.35(5)	C(35)–C(36)	1.40(5)
C(14)–C(15)	1.69(6)	C(36)–C(37)	1.55(5)
C(15)–C(16)	1.41(6)	C(37)–C(38)	1.43(5)
C(16)–C(17)	1.33(6)	C(38)–C(39)	1.36(5)
C(17)–C(13)	1.55(5)	C(39)–C(35)	1.54(5)
C(8)–C(18)	1.63(5)	C(30)–C(40)	1.56(5)
C(18)–C(19)	1.46(5)	C(40)–C(41)	1.51(5)
C(19)–C(20)	1.59(6)	C(41)–C(42)	1.49(6)
C(20)–C(21)	1.40(6)	C(42)–C(43)	1.29(6)
C(21)–C(22)	1.49(6)	C(43)–C(44)	1.47(5)
C(22)–C(18)	1.45(5)	C(44)–C(40)	1.37(5)

(*b*) Bond angles

C(1)–W(1)–C(2)	78(2)	C(23)–W(2)–C(24)	82(2)
W(1)–C(1)–O(1)	178(3)	W(2)–C(23)–O(3)	173(3)
W(1)–C(2)–O(2)	161(3)	W(2)–C(24)–O(4)	163(5)
C(3)–C(4)–C(5)	110(4)	C(25)–C(26)–C(27)	105(5)
C(4)–C(5)–C(6)	98(4)	C(26)–C(27)–C(28)	103(5)
C(5)–C(6)–C(7)	116(5)	C(27)–C(28)–C(29)	108(6)
C(6)–C(7)–C(3)	94(4)	C(28)–C(29)–C(25)	107(7)
C(7)–C(3)–C(4)	115(4)	C(29)–C(25)–C(26)	117(7)
C(8)–C(9)–C(10)	102(3)	C(30)–C(31)–C(32)	108(3)
C(9)–C(10)–C(11)	108(3)	C(31)–C(32)–C(33)	100(3)
C(10)–C(11)–C(12)	113(3)	C(32)–C(33)–C(34)	118(3)
C(11)–C(12)–C(13)	112(3)	C(33)–C(34)–C(30)	101(3)
C(12)–C(8)–C(9)	109(3)	C(34)–C(30)–C(31)	105(2)
C(11)–C(12)–C(13)	112(3)	C(33)–C(34)–C(35)	108(3)
C(8)–C(12)–C(13)	117(3)	C(30)–C(34)–C(35)	112(3)
C(12)–C(13)–C(17)	123(4)	C(34)–C(35)–C(36)	124(4)
C(12)–C(13)–C(14)	127(4)	C(34)–C(35)–C(39)	128(3)
C(13)–C(14)–C(15)	103(4)	C(35)–C(36)–C(37)	108(4)
C(14)–C(15)–C(16)	104(4)	C(36)–C(37)–C(38)	103(4)
C(15)–C(16)–C(17)	113(5)	C(37)–C(38)–C(39)	116(4)
C(16)–C(17)–C(13)	109(4)	C(38)–C(39)–C(35)	104(3)
C(17)–C(13)–C(14)	111(4)	C(39)–C(35)–C(36)	109(3)
C(9)–C(8)–C(18)	104(3)	C(31)–C(30)–C(40)	109(3)
C(12)–C(8)–C(18)	112(3)	C(34)–C(30)–C(40)	114(3)
C(8)–C(18)–C(19)	121(3)	C(30)–C(40)–C(41)	121(4)
C(8)–C(18)–C(22)	120(3)	C(30)–C(40)–C(44)	127(4)
C(18)–C(19)–C(20)	94(4)	C(40)–C(41)–C(42)	103(4)
C(19)–C(20)–C(21)	116(5)	C(41)–C(42)–C(43)	107(5)
C(20)–C(21)–C(22)	106(5)	C(42)–C(43)–C(44)	116(5)
C(21)–C(22)–C(18)	104(4)	C(43)–C(44)–C(40)	103(4)
C(22)–C(18)–C(19)	111(4)	C(44)–C(40)–C(41)	111(4)
Cent.[a] W(1)–C(1)	121	Cent.[b] W(2)–C(23)	117
Cent.[a] W(1)–C(2)	120	Cent.[b] W(2)–C(24)	125
Cent.[a] W(1)–C(10)	113	Cent.[b] W(2)–C(32)	113

[a] Centroid of the cyclopentadienyl ring comprised of C(3)–C(7). [b] Centroid of the cyclopentadienyl ring comprised of C(25)–C(29).

For the central carbon atoms the W–C(η^3) lengths are 2.16(3) and 2.18(3) Å (Table 2) while the average for the remaining ones is 2.36 Å. A similar situation is found in related compounds: 2.30 compared to 2.42 Å in [W(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)],[2] 2.26 and 2.45 Å in [W(CO)$_2$(η^5-C$_9$H$_7$)(η^3-C$_9$H$_7$)],[12] and 2.07 and 2.29 Å in [W(CO)$_2$(η^3-C$_3$H$_5$)(O$_2$CCF$_3$){CH$_3$O(CH$_2$)$_2$OCH$_3$}].[13] With the latter, both the W–C(η^3) distances are short, presumably because of the effect of the other small, electronegative ligands. In the title compound the W–C(η^3) bond to the unique carbon atom is close to the W–C(σ) length in compounds such as [WMe$_2$(NEt$_2$)$_4$],[14] 2.17 Å, and [W$_2$(CH$_2$SiMe$_3$)$_6$],[15] 2.14 Å. The bonds to the remaining carbon atoms of the η^3 ligand are near the normal value for the W–C(η^5) bonds.

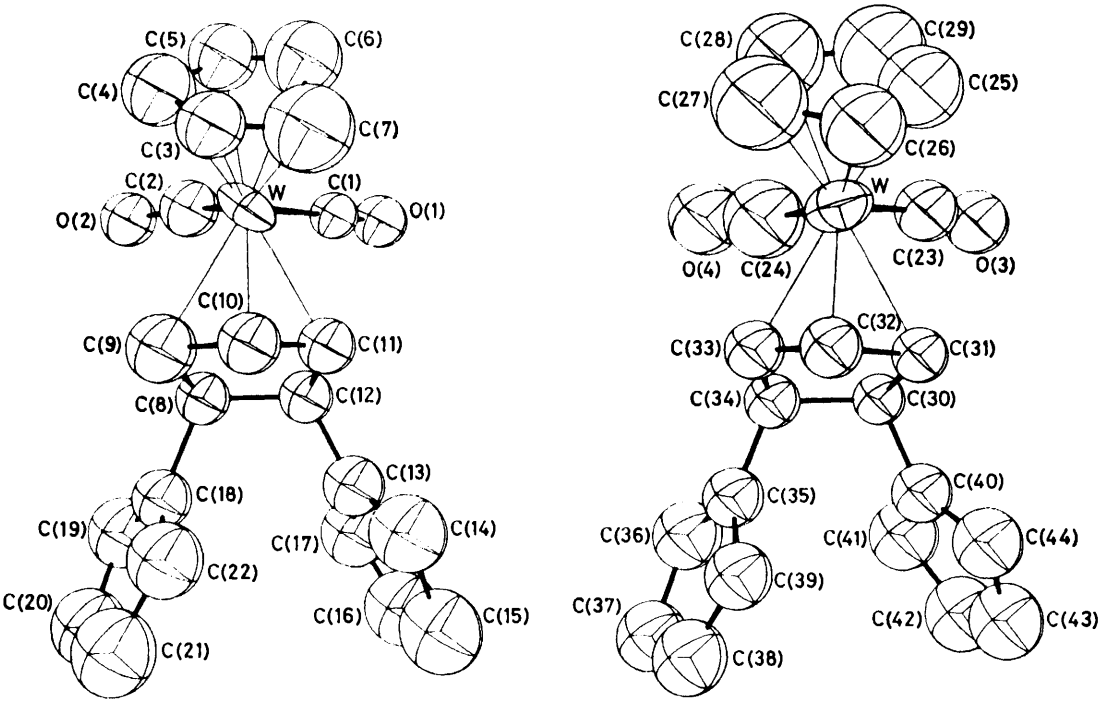
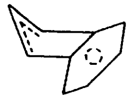
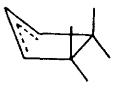


FIGURE 1 Molecular structures and atom-numbering schemes for the two crystallographically independent molecules of [W(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_{15}$H$_{15}$)]

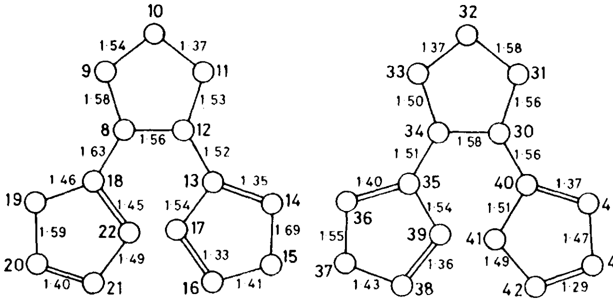
In the two independent molecules the plane of the allylic group makes angles of 25 and 28° with the plane of the ring carbons excluding the unique carbon atom. This can be compared to related values of 26° in [W(CO)$_2$(η^5-C$_9$H$_7$)(η^3-C$_9$H$_7$)] [12] and 20° in [W(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)].[2] The explanation for the larger average value (26.5°) for the title compound lies in a detailed consideration of the η^3 ligands themselves [(1), (2), and (3)]. Even though the three compounds are very similar with respect to the environment about the metal atom, there is an important difference in the η^3 moieties. In (1) and (2) the carbon atoms of the η^3-C$_5$ unit which are not bonded to the tungsten atom are sp^2 hybridized. In (3), they are sp^3 hybridized. The larger angle for [W(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_{15}$H$_{15}$)] may be attributed to the non-bonded interaction of the hydrogen atoms shown in (3) with the carbonyl groups. [If one takes (3) as the standard, the change to sp^2 hybridization in (1) or (2) has the effect of moving the analogous atoms away from the carbonyl ligands.]


(1)


(2)


(3)

The C$_5$H$_5$ groups bonded to the sp^3 hybridized carbon atoms of the η^3-C$_5$H$_5$ rings are dienes, but differ in the location of the tetrahedral carbon atoms. It exists in the 2 position on one and the 3 position on the other. A comparison is given in (4) and (5). Although the standard deviations are so large that the differences are of marginal significance, the fact that two independent molecules show the same pattern lends credence to the description.



(4) (5)

FIGURE 2 Comparison of the two independent C$_{15}$H$_{15}$ ligands with the bond lengths (Å) given

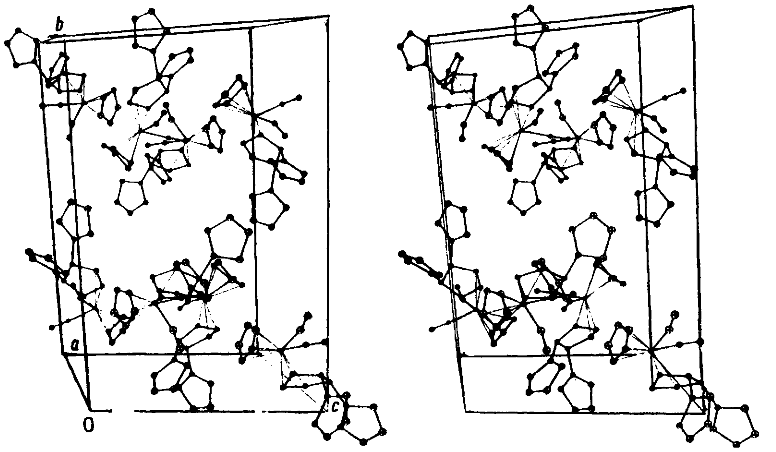
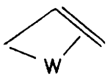


FIGURE 3 Stereoscopic view of the unit-cell packing in $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_{15}H_{15})]$

A further point of interest in (4) and (5) (Figure 2) concerns the bond lengths in the allyl portion of the $C_{15}H_{15}$ ligand. It would appear that a substantial localization of π-electron density exists between C(10) and C(11) and again between C(32) and C(33). This would lead to a view of the η^3 co-ordination as in (6).



(6)

The η^5-C_5H_5 ligand appears normal in all respects. The W–C bond lengths range from 2.24(4) to 2.43(3) Å, and average 2.32(6) Å. This agrees well with the 2.31—2.47 Å range and 2.37 Å average in $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$,[2] and the 2.34 Å average in $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$.[16]

A stereoscopic view of the unit-cell packing is shown in Figure 3. No unusually short intermolecular separations are noted.

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