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Structure of Pentacarbonyl[3-(1,1-diphenylvinyl)cyclopentyl]ethoxymethylenetungsten(0)

BY JEAN-CLAUDE DARAN AND YVES JEANNIN

Laboratoire de Chimie des Métaux de Transition, ERA 608, *Université Pierre et Marie Curie,* 4 *place Jussieu,*
75230 *Paris CEDEX* 05, *France*

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Abstract

$[W(CO)_5\{C(OC_2H_5)[C_5H_8CHC(C_6H_5)_2]\}]$, $C_{27}H_{24}O_6W$, $M_r = 627{\cdot}9$, monoclinic, $C2/c$, $a = 47{\cdot}52\,(2)$, $b = 6{\cdot}421\,(3)$, $c = 16{\cdot}757\,(5)$ Å, $\beta = 90{\cdot}82\,(3)°$, $V = 5106$ Å^3, $D_m = 1{\cdot}63\,(2)$, $D_x = 1{\cdot}63$ Mg m^{-3}, $Z = 8$. The final $R_w = 0{\cdot}053$ for 2832 independent reflexions. The cell contains discrete molecular units of $[W(CO)_5\{C(OC_2H_5)[C_5H_8CHC(C_6H_5)_2]\}]$. The W=C distance is 2·18 (2) Å. The unsaturated moiety is oriented in such a way that phenyl rings point away from the W atom.

Introduction

In order to gain insight into the role of transition-metal carbene complexes in the catalysis of olefin metathesis, Levisalles and co-workers studied new compounds of the type $(CO)_5W{-}CRR'$ where R and R' are alkyl groups. Reaction of $(CO)_5W{=}C\begin{smallmatrix}\diagup\varphi\\ \diagdown\varphi\end{smallmatrix}$ with 2-ethoxynorbornene gives a new compound, $[(CO)_5W{=}C(OC_2H_5)\{(C_5H_8)CHC\varphi_2\}]$, whose crystal structure we report. This work has been the subject of a preliminary communication (Levisalles, Rudler, Villemin, Daran, Jeannin & Martin, 1978), in which it was underlined that data were collected on a Nonius CAD-3 diffractometer with Cu $K\alpha$ radiation. Inconsistencies in interatomic distances and angles proved this first set of data to be of poor quality, and the need for the data collection to be resumed.

Upon exposure to air, the crystals rapidly lost their ability to diffract, presumably through slow decomposition, so they were mounted under dry argon in Lindemann-glass capillaries. Symmetry and systematic absences (hkl, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$) consistent with the monoclinic space group $C2/c$ were observed from precession photographs. A parallelepiped (0·1 × 0·14 × 0·34 mm) was set up on an automatic three-circle diffractometer built in the laboratory, about its [010] axis. Cell parameters were obtained by least-squares analysis of nine centered reflexions, and values agree fairly well with those given in the preliminary communication. D_c was measured by flotation in tetrabromoethane/dibromoethane mixtures.

The intensity of every independent reflexion with $\sin\theta/\lambda < 0{\cdot}55$ Å^{-1} was measured by a $\theta/2\theta$ scan at room temperature. Mo $K\alpha$ radiation from a graphite monochromator set in front of the counter was used; the take-off angle was 2·5°. A scan range of $0{\cdot}47° + 0{\cdot}345° \tan\theta$ was used with a scan speed of 1·25° min^{-1}. Background was measured for 10 s at both ends of a scan in fixed position. The intensities of two standard reflexions (004 and 16,0,0) were monitored every 100 reflexions; no significant fluctuations were observed. Lorentz and polarization corrections were applied, together with an absorption correction (Wehe, Busing & Levy, 1962) ($\mu = 4{\cdot}84$ mm^{-1}). Each structure factor was assigned a standard deviation $\sigma = (F\Delta I)/I$ where I was the integrated intensity and ΔI the error. Of the 3534 independent reflexions, 702 with $F < \sigma(F)$ were not included in subsequent calculations.

Computations were performed with standard programs. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974), including f' and f'' for W. The agreement factors were defined as $R = \sum(|F_o - F_c|)/\sum|F_o|$ and $R_w = [\sum|w(F_o - F_c)|^2/\sum(wF_o)^2]^{1/2}$. A weighting scheme based on counting statistics, $w = 2F/\sigma$, was used.

The W atom was located from a Patterson function. O and C atoms were found from a heavy-atom-phased F_o synthesis. Atomic positions were refined by full-matrix least squares, first with isotropic then anisotropic temperature factors. H atoms were found on a difference map, and included as a fixed contribution at their calculated idealized positions (C—H = 1·0 Å). They were assigned thermal parameters 1·0 Å^2 higher than those of the C atoms to which they are attached. The final refinement of 307 variables with 2382 observations resulted in $R = 0{\cdot}056$ and $R_w = 0{\cdot}053$.

Final atomic coordinates for all non-hydrogen atoms are reported in Table 1.* Bond distances and angles,

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35048 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (×10⁴) *of the nonhydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
W	1824·1 (1)	2752·1 (7)	−3514·8 (3)
C(1)	1678 (3)	5401 (21)	−4028 (7)
O(1)	1600 (3)	6894 (17)	−4332 (7)
C(2)	2004 (3)	86 (22)	−3045 (9)
O(2)	2108 (3)	−1379 (19)	−2829 (8)
C(3)	1433 (3)	1460 (22)	−3614 (11)
O(3)	1215 (3)	808 (22)	−3706 (10)
C(4)	1909 (4)	1454 (25)	−4599 (11)
O(4)	1963 (4)	747 (22)	−5189 (8)
C(5)	2215 (4)	4031 (22)	−3518 (9)
O(5)	2438 (3)	4640 (21)	−3575 (9)
C(6)	1699 (3)	4021 (24)	−2367 (8)
O(6)	1831 (2)	4118 (20)	−1687 (6)
C(7)	2120 (3)	3307 (32)	−1574 (10)
C(8)	2241 (5)	4266 (37)	−845 (13)
C(9)	1415 (3)	5075 (30)	−2250 (9)
C(10)	1227 (4)	4008 (27)	−1606 (10)
C(11)	1099 (3)	5801 (23)	−1144 (8)
C(12)	1340 (3)	7400 (30)	−1106 (10)
C(13)	1452 (4)	7354 (31)	−1940 (12)
C(14)	992 (3)	5248 (23)	−346 (8)
C(15)	751 (2)	5864 (19)	7 (7)
C(16)	548 (2)	7294 (20)	−394 (6)
C(17)	274 (3)	6727 (23)	−537 (8)
C(18)	85 (3)	8084 (31)	−918 (9)
C(19)	177 (4)	10060 (31)	−1104 (10)
C(20)	448 (4)	10640 (28)	−979 (11)
C(21)	634 (3)	9331 (23)	−622 (9)
C(22)	675 (3)	5139 (23)	818 (7)
C(23)	515 (3)	6436 (26)	1307 (8)
C(24)	436 (3)	5763 (33)	2075 (8)
C(25)	516 (3)	3824 (34)	2320 (8)
C(26)	668 (3)	2526 (30)	1856 (8)
C(27)	748 (3)	3172 (23)	1091 (8)

Table 2. *Bond distances* (Å) *and angles* (°) *around the* W *atom with e.s.d.'s in parentheses*

W—C(1)	2·02 (1)	C(1)—W—C(2)	175·1 (5)
W—C(2)	2·06 (2)	C(1)—W—C(3)	90·2 (5)
W—C(3)	2·04 (2)	C(1)—W—C(4)	92·0 (6)
W—C(4)	2·04 (2)	C(1)—W—C(5)	88·0 (6)
W—C(5)	2·03 (2)	C(1)—W—C(6)	88·0 (5)
W—C(6)	2·18 (1)	C(2)—W—C(3)	93·7 (6)
		C(2)—W—C(4)	85·1 (6)
C(1)—O(1)	1·14 (2)	C(2)—W—C(5)	87·9 (6)
C(2)—O(2)	1·12 (2)	C(2)—W—C(6)	95·1 (6)
C(3)—O(3)	1·13 (2)	C(3)—W—C(4)	87·3 (7)
C(4)—O(4)	1·12 (2)	C(3)—W—C(5)	175·1 (7)
C(5)—O(5)	1·13 (2)	C(3)—W—C(6)	88·0 (7)
		C(4)—W—C(5)	88·3 (6)
W—C(1)—O(1)	179 (1)	C(4)—W—C(6)	175·3 (6)
W—C(2)—O(2)	176 (1)	C(5)—W—C(6)	96·4 (6)
W—C(3)—O(3)	176 (1)		
W—C(4)—O(4)	178 (1)		
W—C(5)—O(5)	174 (1)		

with e.s.d.'s calculated from the full variance–covariance matrix, are given in Table 2 and Fig. 1, and the equations of important molecular planes in Table 3.

Table 3. *Equations of least-squares planes and displacements* (Å) *of specified atoms from the planes*

In the equations, x, y and z represent fractional coordinates with respect to the crystallographic axes.

Plane 1: W, C(6), O(6), C(9)

$$18\cdot776x + 5\cdot674y - 4\cdot284z = 6\cdot492$$

W	0·000 (5)	O(6)	0·005 (13)
C(6)	−0·007 (15)	C(9)	0·009 (19)

Plane 2: W, C(1), C(2), C(4)

$$43\cdot130x + 2\cdot666y + 0\cdot404z = 8\cdot459$$

W	−0·0002 (5)	C(4)	−0·023 (17)
C(1)	0·057 (13)	C(6)	−0·1542 (22)
C(2)	0·085 (14)		

Plane 3: C(3), C(4), C(5), C(6)

$$16\cdot413x - 5\cdot263y + 7\cdot569z = -1\cdot133$$

C(3)	−0·018 (15)	C(6)	0·015 (15)
C(4)	0·021 (16)	W	0·018 (20)
C(5)	−0·015 (15)		

Plane 4: ring C(9), C(10), C(11), C(12), C(13)

$$33\cdot435x - 2\cdot482y - 9\cdot800z = 1\cdot307$$

C(9)	−0·04 (2)	C(12)	0·25 (2)
C(10)	0·23 (2)	C(13)	−0·18 (2)
C(11)	−0·19 (1)		

Plane 5: C(9), C(10), C(12), C(13)

$$40\cdot163x - 2\cdot120y + 6\cdot795z = 3\cdot027$$

C(9)	0·053 (16)	C(13)	−0·073 (18)
C(10)	−0·041 (18)	C(11)	−0·619 (23)
C(12)	0·034 (15)		

Plane 6: C(14), C(15), C(16), C(22)

$$22\cdot485x + 5\cdot036y + 6\cdot593z = 4\cdot646$$

C(14)	0·000 (14)	C(16)	0·000 (12)
C(15)	0·000 (12)	C(22)	0·000 (14)

Plane 7: ring C(16) to C(21)

$$12\cdot868x - 2\cdot234y - 15\cdot102z = -0\cdot331$$

C(16)	0·002 (10)	C(19)	−0·022 (18)
C(17)	−0·009 (13)	C(20)	0·009 (18)
C(18)	0·020 (16)	C(21)	0·000 (15)

Plane 8: ring C(22) to C(27)

$$39\cdot856x + 2\cdot426y + 6\cdot323z = 4\cdot447$$

C(22)	0·008 (13)	C(25)	0·003 (17)
C(23)	−0·006 (15)	C(26)	0·003 (15)
C(24)	−0·001 (16)	C(27)	−0·008 (14)

Angles between planes (°)

1–2	44·2 (1·5)	6–7	59·8 (1·3)
1–3	45·5 (1·5)	6–8	31·8 (0·7)
2–3	90·5 (0·4)		

Discussion

The crystal consists of discrete molecular units of $[W(CO)_5\{C(OC_2H_5)[C_5H_8CHC(C_6H_5)_2]\}]$ separated by normal van der Waals distances. As shown in Fig. 2, W is octahedrally coordinated to the C atoms, the five carbonyl groups and the carbene group. The molecule is the insertion product of the diphenyltungstacarbene into the double bond of the 2-ethoxy-

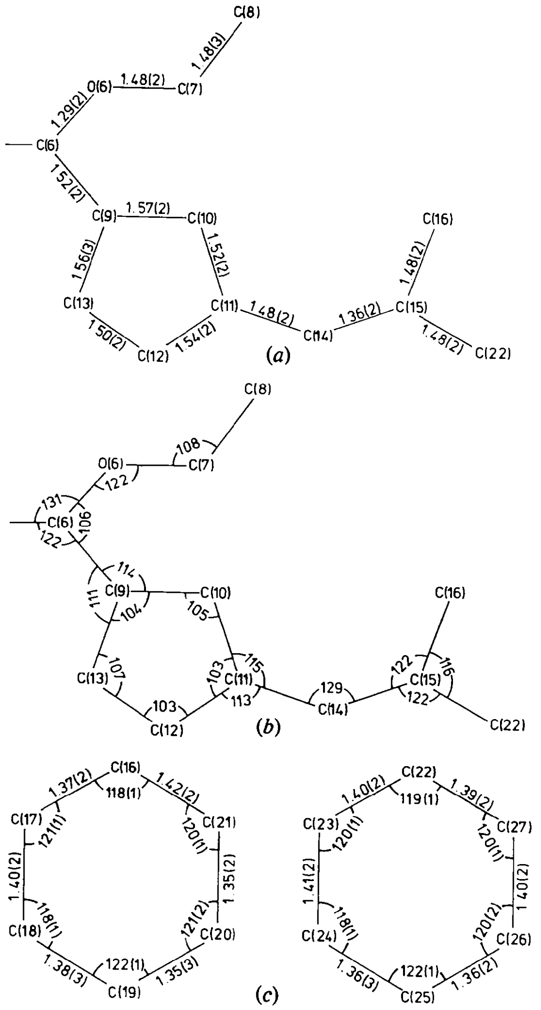

Fig. 1. Intramolecular dimensions of the [3-(1,1-diphenylvinyl)-cyclopentyl]ethoxymethylene moiety. (*a*) Bond distances (Å); (*b*) bond angles (°) [C(15)–C(16)–C(17), 122 (1); C(15)–C(16)–C(21), 120 (1); C(15)–C(22)–C(23), 119 (1); C(15)–C(22)–C(27), 122 (1)] (average e.s.d. 1°); (*c*) bond distances and angles in the phenyl groups.

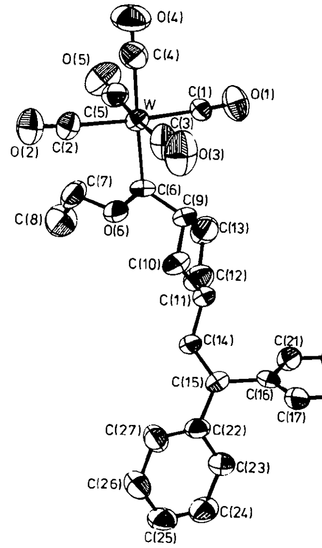

Fig. 2. *ORTEP* view (Johnson, 1965) of the molecule with the atom numbering. The ellipsoids represent 50% electron probability.

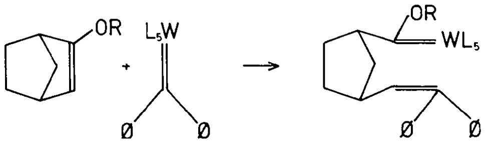

Fig. 3. The insertion reaction.

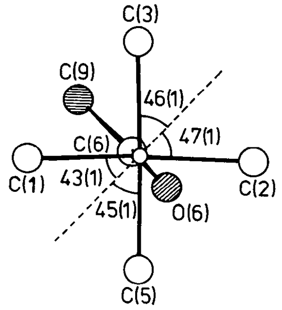

Fig. 4. Projection on to the best plane C(1), C(2), C(3), C(5). Angles are given in degrees.

norbornene, Fig. 3. The most striking feature of this structure is the fact that the carbene and the unsaturated moiety of the complex are as far as possible from each other.

The length of the tungsten–carbene carbon bond, W–C(6), 2·18 (2) Å, is somewhat longer than the 2·14 (2) Å (mean value) found in [$W(CO)_5\{C(C_6H_5)_2\}$] (Casey, Burkhardt, Bunnell & Calabrese, 1977). This may be due solely to the better π-donor ability of oxygen with respect to a phenyl group. The interaction between a lone pair on the O atom with the empty *p* orbital of the carbene C atom will compete with the back donation from the metal and may account for a decrease of the W=C bond. This interpretation agrees with the short C(6)–O(6) length, 1·29 (2) Å, which is close to the 1·33 Å observed in [$Cr(CO)_5\{C(OCH_3)(C_6H_5)\}$] (Mills & Redhouse, 1968). The carbene C(6) and the atoms bonded to it, W, O(6), C(9), are coplanar (Table 3). The normal to this plane almost bisects the directions of the equatorial carbonyl groups of the W octahedron, making angles of 43 (1), 45 (1), 47 (1) and 46 (1)° (Fig. 4). A similar conformation exists in [$Cr(CO)_5\{C(OCH_3)(C_6H_5)\}$]. The average W to CO length of 2·04 Å can be compared to 2·02 Å in [$W(CO)_5\{C(C_6H_5)_2\}$].

Table 4. *Torsion angles* (°) *in the cyclopentane ring*

φ_0	C(13)–C(9)–C(10)–C(11)	16·62 (2)
φ_1	C(9)–C(10)–C(11)–C(12)	−36·99 (4)
φ_2	C(10)–C(11)–C(12)–C(13)	43·56 (4)
φ_3	C(11)–C(12)–C(13)–C(9)	−33·02 (1)
φ_4	C(12)–C(13)–C(9)–C(10)	10·37 (2)

Conformation parameter (phase angle of pseudorotation): $\Delta = 135°$; $\tan \Delta/2 = (\varphi_2 + \varphi_4) - (\varphi_1 + \varphi_3)/2\varphi_0\,(\sin 36° + \sin 72°)$ (Altona, Geise & Romers, 1968)

The values of the torsion angles (Table 4) in the cyclopentane ring [C(9) to C(13)] indicate a conformation intermediate between a half-chair and an envelope (Gallen, Carrell, Zacharias, Glusker & Stephani, 1975), with a maximum puckering at C(11). The C—C distances of 1·53 Å (mean value) and the C—C—C angles of 105° (mean value) fall within the range of values found for other cyclopentane rings (Altona, Geise & Romers, 1968).

Both phenyl groups are planar and form angles of 59·8 and 31·8° with the C(14), C(15), C(16), C(22) plane. Steric interactions prevent the phenyl rings from being coplanar with this plane. The average C—C distance is 1·38 Å with no systematic variations, and C—C—C angles range from 118 to 122°.

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The Structure of Bis(diphenylphosphinoacetato)palladium(II)

By S. Civiš, J. Podlahová* and J. Loub

Department of Inorganic Chemistry, Charles University, Albertov 2030, 12840 *Praha* 2, *Czechoslovakia*

and J. Ječný

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Heyrovský Square 2,
16206 *Praha* 6, *Czechoslovakia*

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Abstract

$C_{28}H_{24}O_4P_2Pd$, $[Pd(C_{14}H_{12}O_2P)_2]$, is monoclinic, space group $P2_1/c$, with $a = 9{\cdot}494\ (3)$, $b = 23{\cdot}66\ (1)$, $c = 12{\cdot}673\ (3)$ Å, $\beta = 116{\cdot}33\ (2)°$, $Z = 4$. The structure was refined to $R = 0{\cdot}048$ for 2664 counter reflections $[I > 1{\cdot}96\sigma(I)]$. The Pd atom is surrounded in a distorted *cis* square-planar arrangement by two P [Pd—P 2·235 (2) Å] and two O atoms [Pd—O 2·076 (5) Å] belonging to two chelating diphenylphosphinoacetato anions.

Introduction

Spectral and other indirect evidence (Růžičková & Podlahová, 1978; Podlahová & Podlaha, 1979) indicate that phosphinoacetic acids and their anions can bond to transition-metal ions as unidentate (P or O) or chelating (P, O) ligands. The unidentate P coordination was confirmed by the structure determination of dibromobis(diphenylphosphinoacetic acid)palladium(II) (Podlahová, Loub & Ječný, 1979). As the properties of the related complex, bis(diphenylphosphinoacetato)palladium(II), indicated the presence of chelating ligands, the structure determination of this

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* To whom correspondence should be addressed.

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