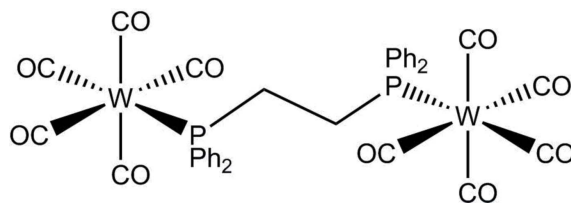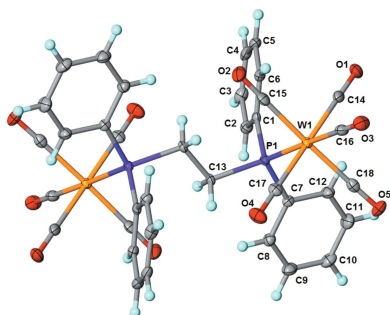# Crystal structure of (OC)$_5$W(μ-dppe)W(CO)$_5$

Hannah F. Drake,[a] Kraig A. Wheeler[b] and Brian J. Bellott[a]*

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The centrosymmetric title complex, [μ-ethane-1,2-diylbis(diphenylphosphane)-$\kappa^2 P$:P']bis[pentacarbonyltungsten(0)], [W$_2$(C$_{26}$H$_{24}$P$_2$)(CO)$_{10}$], consists of two W(CO)$_5$ moieties bridged by a bis(diphenylphosphanyl)ethane (dppe) ligand. The W^0 atom has a slightly distorted octahedral coordination environment consisting of 5 carbonyl ligands and one P atom from the bridging dppe ligand with the nearest W^0 atom 5.625 (5) Å away. The complex resides on a center of symmetry.

1. Chemical context

In 1976, Pickett and Pletcher studied the mechanism of reduction of a group 6 carbonyl complex in the presence of carbon dioxide (Pickett & Pletcher, 1976). Recently Grice & Saucedo (2016) have shown that group 6 metal–carbonyl complexes without 'non-innocent' ligands can electro-catalytically reduce CO$_2$. Dickson *et al.* (1989) varied the ligand Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2, 4, and 5), finding that the predominate product in the reactions of n = 2 and 5 is the bridged complex (OC)$_5$W[μ-Ph$_2$P(CH$_2$)$_n$]PPh$_2$)W(CO)$_5$, whereas when n = 4 it was reported the chelated product is favored (W(CO)$_4$[μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$]). Tan *et al.* (1994) reported the separation of several diphosphine-bridged group 6 decacarbonyl complexes by HPLC, but no further characterization was reported. Keiter *et al.* (1981) and Gan *et al.* (1993) have reported group 6 heterobimetallic complexes using dppe as the bridging ligand. The title complex has been reported by Keiter & Shah (1972), Ozer *et al.* (1993), and El-Khateeb *et al.* (2002), but the structure has yet to be published. We report here its single crystal X-ray structure determination.

2. Structural commentary

The molecular structure of (OC)$_5$W(μ-dppe)W(CO)$_5$ (Fig. 1) consists of two six-coordinate tungsten(0) atoms, each in a slightly distorted octahedral environment. The coordination environment of tungsten has five carbonyl ligands and one phosphorus atom from the dppe ligand. The axial carbonyl
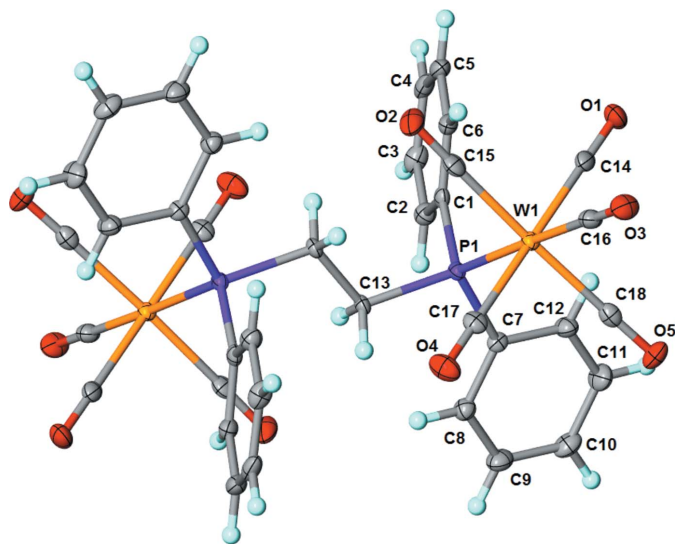
Figure 1
The molecular structure of (OC)$_5$W(μ-Ph$_2$PCH$_2$CH$_2$PPh$_2$)W(CO)$_5$ with displacement ellipsoids drawn at 50% probability level for non-H atoms and H atoms shown as spheres of arbitrary size. Non-labelled atoms are generated by the symmetry operation $-x$, $-y + 1$, $-z + 1$.

ligands have a bond length of 2.015 (3) Å and the average bond length for the equatorial carbonyl ligands is 2.048 (8) Å. The W1—P1 bond length is 2.5200 (8) Å and the P1—W1—C(axial) bond angle is 178.79 (9)°. The average P1—W1—C(equatorial) bond angle is 90.10 (18)°. Examination of the dppe backbone shows the P1—C13 bond length at 1.843 (3) Å and the C13—C13 bond length at 1.531 (6) Å. The molecule sits on a center of symmetry.

3. Supramolecular features

The two tungsten atoms in each of the molecules (OC)$_5$W(μ-dppe)W(CO)$_5$ are bridged by a diphosphine approximately along the c axis and the molecules themselves are stacked along the a axis. No significant van der Waals-type interactions such as C—H$\cdots\pi$ or π–π contacts between adjacent molecules are observed.

4. Database survey

A search of the database for homonuclear decacarbonyl group 6 complexes bridged by symmetric phosphines yielded four complexes. There are two tungsten complexes (OC)$_5$W[μ-Ph$_2$P(CH$_2$)$_5$PPh$_2$]W(CO)$_5$ (Ueng & Shih, 1995), (OC)$_5$W(μ-Ph$_2$PCH$_2$PPh$_2$)W(CO)$_5$ (Benson et al., 1998), one molybdenum complex (OC)$_5$Mo[μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$]Mo(CO)$_5$ (Alyea et al., 1990), and one chromium complex (OC)$_5$Cr[μ-Ph$_2$P(CH$_2$)$_5$PPh$_2$]Cr(CO)$_5$ (Ueng & Shih, 1995).

5. Synthesis and crystallization

All synthesis and crystallization procedures were carried out using standard Schlenk techniques. Dichloromethane was

Table 1
Experimental details.

Crystal data	
Chemical formula	[W$_2$(C$_{26}$H$_{24}$P$_2$)(CO)$_{10}$]
M_r	1046.17
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.8193 (4), 16.0492 (7), 11.3312 (5)
β (°)	96.511 (2)
V (Å^3)	1774.19 (13)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	13.15
Crystal size (mm)	0.15 × 0.14 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2011)
T_{min}, T_{max}	0.254, 0.756
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26419, 3256, 2954
R_{int}	0.056
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.048, 1.06
No. of reflections	3256
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.58

Computer programs: APEX2 and SAINT (Bruker, 2011), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b) and X-SEED (Barbour, 2001).

added to a mixture of W(CO)$_5$(NH$_2$C$_6$H$_5$) (0.10 g, 2.9 mmol) and dppe (0.12 g, 3.0 mmol) to produce a golden yellow solution. After two h, methanol was added to precipitate a yellow solid. The precipitate was collected and washed with methanol (3 x 20 mL). The resulting yellow solid was recrystallized from a 1:5 mixture of dichloromethane:methanol at 253 K.

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. The phenyl H-atom positions and the methylene H atoms on the ligand backbone have been positioned according to idealized C—H distances.

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Crystal structure of (OC)₅W(*μ*-dppe)W(CO)₅

Hannah F. Drake, Kraig A. Wheeler and Brian J. Bellott

Computing details

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT* (Bruker, 2011); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED* (Barbour, 2001).

[*μ*-Ethane-1,2-diylbis(diphenylphosphane)-*κ²P:P′*]bis[pentacarbonyltungsten(0)]

Crystal data

[W₂(C₂₆H₂₄P₂)(CO)₁₀]	$F(000) = 996$
$M_r = 1046.17$	$D_x = 1.958$ Mg m⁻³
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 9.8193$ (4) Å	Cell parameters from 8094 reflections
$b = 16.0492$ (7) Å	$\theta = 4.6$–66.6°
$c = 11.3312$ (5) Å	$\mu = 13.15$ mm⁻¹
$\beta = 96.511$ (2)°	$T = 100$ K
$V = 1774.19$ (13) Å³	Transparent rhomboid, colorless
$Z = 2$	$0.15 \times 0.14 \times 0.06$ mm

Data collection

Bruker APEXII CCD diffractometer	3256 independent reflections
Detector resolution: 8.33 pixels mm⁻¹	2954 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.056$
Absorption correction: multi-scan (SADABS; Bruker, 2011)	$\theta_{max} = 68.2°$, $\theta_{min} = 4.8°$
	$h = -11 \rightarrow 11$
	$k = -19 \rightarrow 19$
$T_{min} = 0.254$, $T_{max} = 0.756$	$l = -13 \rightarrow 13$
26419 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.021$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.5664P]$
$wR(F^2) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3256 reflections	$\Delta\rho_{max} = 0.54$ e Å⁻³
226 parameters	$\Delta\rho_{min} = -0.58$ e Å⁻³
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All nonhydrogen atoms were located in a single difference Fourier electron density maps and refined using anisotropic diplacement parameters. All C-H hydrogen atoms were placed in calculated positions with Uiso = 1.2xUeqiv of the connected C atoms

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
W1	0.17092 (2)	0.47944 (2)	0.81902 (2)	0.01462 (6)
P1	0.15114 (8)	0.56563 (5)	0.63197 (7)	0.01359 (16)
O1	0.1345 (2)	0.64362 (16)	0.9701 (2)	0.0277 (6)
O2	−0.1519 (2)	0.44991 (18)	0.7958 (2)	0.0324 (6)
O3	0.2025 (2)	0.36975 (16)	1.0520 (2)	0.0286 (6)
O4	0.2103 (3)	0.31759 (16)	0.6641 (2)	0.0317 (6)
O5	0.4947 (2)	0.50864 (15)	0.8560 (2)	0.0274 (6)
C1	0.0518 (3)	0.66234 (19)	0.6298 (3)	0.0162 (6)
C2	0.0733 (3)	0.7262 (2)	0.5503 (3)	0.0206 (7)
H2	0.1383	0.7188	0.4950	0.025*
C3	0.0010 (3)	0.8002 (2)	0.5510 (3)	0.0251 (8)
H3	0.0155	0.8429	0.4958	0.030*
C4	−0.0924 (3)	0.8119 (2)	0.6323 (3)	0.0253 (8)
H4	−0.1402	0.8633	0.6342	0.030*
C5	−0.1164 (3)	0.7490 (2)	0.7106 (3)	0.0238 (7)
H5	−0.1813	0.7571	0.7657	0.029*
C6	−0.0453 (3)	0.6737 (2)	0.7089 (3)	0.0196 (7)
H6	−0.0633	0.6301	0.7618	0.023*
C7	0.3146 (3)	0.60406 (19)	0.5907 (3)	0.0149 (6)
C8	0.3683 (3)	0.5823 (2)	0.4868 (3)	0.0202 (7)
H8	0.3191	0.5455	0.4319	0.024*
C9	0.4940 (3)	0.6143 (2)	0.4630 (3)	0.0264 (8)
H9	0.5300	0.5991	0.3917	0.032*
C10	0.5671 (3)	0.6679 (2)	0.5420 (3)	0.0260 (8)
H10	0.6532	0.6892	0.5256	0.031*
C11	0.5130 (4)	0.6903 (2)	0.6460 (3)	0.0269 (8)
H11	0.5614	0.7280	0.7001	0.032*
C12	0.3894 (3)	0.6578 (2)	0.6706 (3)	0.0218 (7)
H12	0.3546	0.6722	0.7428	0.026*
C13	0.0738 (3)	0.51389 (19)	0.4953 (3)	0.0146 (6)
H13A	0.0747	0.5528	0.4275	0.018*
H13B	0.1297	0.4647	0.4793	0.018*
C14	0.1472 (3)	0.5850 (2)	0.9158 (3)	0.0205 (7)
C15	−0.0363 (4)	0.4607 (2)	0.8030 (3)	0.0213 (7)
C16	0.1906 (3)	0.4096 (2)	0.9678 (3)	0.0207 (7)
C17	0.1959 (3)	0.3754 (2)	0.7191 (3)	0.0202 (7)

| C18 | 0.3793 (4) | 0.4984 (2) | 0.8413 (3) | 0.0205 (7) |

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01547 (9)	0.01626 (9)	0.01235 (9)	−0.00103 (5)	0.00255 (5)	0.00059 (6)
P1	0.0139 (4)	0.0142 (4)	0.0128 (4)	−0.0021 (3)	0.0019 (3)	−0.0009 (3)
O1	0.0315 (14)	0.0288 (14)	0.0221 (13)	0.0051 (11)	−0.0009 (10)	−0.0088 (12)
O2	0.0196 (14)	0.0540 (18)	0.0243 (13)	−0.0101 (12)	0.0050 (10)	0.0027 (13)
O3	0.0304 (14)	0.0356 (15)	0.0209 (13)	0.0049 (11)	0.0071 (10)	0.0106 (12)
O4	0.0430 (16)	0.0231 (14)	0.0311 (14)	−0.0061 (11)	0.0128 (12)	−0.0054 (12)
O5	0.0162 (13)	0.0269 (13)	0.0380 (15)	−0.0008 (10)	−0.0017 (10)	0.0032 (12)
C1	0.0159 (15)	0.0160 (15)	0.0157 (16)	−0.0016 (12)	−0.0030 (12)	−0.0033 (13)
C2	0.0194 (16)	0.0193 (17)	0.0230 (17)	0.0002 (13)	0.0012 (13)	−0.0001 (15)
C3	0.0227 (17)	0.0193 (17)	0.0319 (19)	−0.0013 (14)	−0.0028 (14)	0.0053 (16)
C4	0.0167 (16)	0.0219 (17)	0.035 (2)	0.0033 (14)	−0.0070 (14)	−0.0069 (16)
C5	0.0157 (16)	0.0307 (19)	0.0244 (18)	0.0028 (14)	0.0003 (13)	−0.0076 (16)
C6	0.0157 (15)	0.0255 (18)	0.0170 (16)	0.0007 (13)	0.0001 (13)	−0.0011 (14)
C7	0.0159 (15)	0.0133 (15)	0.0158 (15)	−0.0010 (12)	0.0029 (12)	0.0043 (13)
C8	0.0186 (16)	0.0198 (17)	0.0224 (17)	−0.0024 (13)	0.0027 (13)	0.0000 (14)
C9	0.0210 (17)	0.033 (2)	0.0259 (18)	0.0012 (15)	0.0080 (14)	0.0037 (17)
C10	0.0179 (17)	0.0234 (18)	0.037 (2)	−0.0029 (14)	0.0057 (15)	0.0068 (17)
C11	0.0228 (18)	0.0254 (18)	0.032 (2)	−0.0090 (14)	0.0025 (15)	−0.0033 (17)
C12	0.0184 (16)	0.0236 (18)	0.0243 (18)	−0.0023 (14)	0.0063 (13)	−0.0030 (15)
C13	0.0177 (16)	0.0152 (15)	0.0109 (15)	−0.0028 (12)	0.0007 (12)	−0.0027 (13)
C14	0.0175 (16)	0.0303 (19)	0.0136 (16)	0.0017 (13)	0.0016 (13)	0.0012 (15)
C15	0.029 (2)	0.0228 (18)	0.0132 (16)	−0.0016 (14)	0.0055 (13)	0.0010 (14)
C16	0.0192 (16)	0.0230 (17)	0.0209 (18)	0.0021 (13)	0.0062 (13)	−0.0015 (16)
C17	0.0241 (17)	0.0188 (17)	0.0186 (17)	−0.0033 (13)	0.0067 (13)	0.0024 (15)
C18	0.029 (2)	0.0147 (16)	0.0180 (17)	−0.0001 (14)	0.0025 (14)	0.0002 (14)

Geometric parameters (Å, º)

W1—C16	2.015 (3)	C4—C5	1.381 (5)
W1—C15	2.044 (4)	C4—H4	0.9500
W1—C14	2.045 (4)	C5—C6	1.398 (5)
W1—C17	2.048 (3)	C5—H5	0.9500
W1—C18	2.056 (4)	C6—H6	0.9500
W1—P1	2.5200 (8)	C7—C8	1.388 (4)
P1—C7	1.829 (3)	C7—C12	1.397 (5)
P1—C1	1.832 (3)	C8—C9	1.391 (5)
P1—C13	1.843 (3)	C8—H8	0.9500
O1—C14	1.140 (4)	C9—C10	1.382 (5)
O2—C15	1.143 (4)	C9—H9	0.9500
O3—C16	1.144 (4)	C10—C11	1.394 (5)
O4—C17	1.135 (4)	C10—H10	0.9500
O5—C18	1.139 (4)	C11—C12	1.378 (5)
C1—C6	1.393 (4)	C11—H11	0.9500

C1—C2	1.397 (5)	C12—H12	0.9500
C2—C3	1.384 (5)	C13—C13[i]	1.531 (6)
C2—H2	0.9500	C13—H13A	0.9900
C3—C4	1.385 (5)	C13—H13B	0.9900
C3—H3	0.9500		
C16—W1—C15	89.55 (13)	C4—C5—H5	119.9
C16—W1—C14	91.03 (13)	C6—C5—H5	119.9
C15—W1—C14	89.83 (13)	C1—C6—C5	120.1 (3)
C16—W1—C17	90.16 (13)	C1—C6—H6	120.0
C15—W1—C17	90.64 (13)	C5—C6—H6	120.0
C14—W1—C17	178.72 (13)	C8—C7—C12	118.8 (3)
C16—W1—C18	88.85 (13)	C8—C7—P1	124.1 (2)
C15—W1—C18	178.03 (12)	C12—C7—P1	117.0 (2)
C14—W1—C18	89.05 (13)	C7—C8—C9	120.2 (3)
C17—W1—C18	90.52 (13)	C7—C8—H8	119.9
C16—W1—P1	178.79 (9)	C9—C8—H8	119.9
C15—W1—P1	91.45 (9)	C10—C9—C8	120.7 (3)
C14—W1—P1	89.64 (9)	C10—C9—H9	119.6
C17—W1—P1	89.16 (9)	C8—C9—H9	119.6
C18—W1—P1	90.16 (9)	C9—C10—C11	119.2 (3)
C7—P1—C1	101.08 (14)	C9—C10—H10	120.4
C7—P1—C13	103.13 (14)	C11—C10—H10	120.4
C1—P1—C13	101.69 (14)	C12—C11—C10	120.2 (3)
C7—P1—W1	114.44 (10)	C12—C11—H11	119.9
C1—P1—W1	117.80 (11)	C10—C11—H11	119.9
C13—P1—W1	116.38 (10)	C11—C12—C7	120.8 (3)
C6—C1—C2	118.9 (3)	C11—C12—H12	119.6
C6—C1—P1	120.3 (2)	C7—C12—H12	119.6
C2—C1—P1	120.7 (2)	C13[i]—C13—P1	112.1 (3)
C3—C2—C1	120.7 (3)	C13[i]—C13—H13A	109.2
C3—C2—H2	119.6	P1—C13—H13A	109.2
C1—C2—H2	119.6	C13[i]—C13—H13B	109.2
C2—C3—C4	120.0 (3)	P1—C13—H13B	109.2
C2—C3—H3	120.0	H13A—C13—H13B	107.9
C4—C3—H3	120.0	O1—C14—W1	179.7 (3)
C5—C4—C3	120.1 (3)	O2—C15—W1	179.0 (3)
C5—C4—H4	119.9	O3—C16—W1	179.6 (3)
C3—C4—H4	119.9	O4—C17—W1	179.6 (3)
C4—C5—C6	120.2 (3)	O5—C18—W1	178.7 (3)
C7—P1—C1—C6	−146.7 (3)	W1—P1—C7—C8	117.1 (3)
C13—P1—C1—C6	107.2 (3)	C1—P1—C7—C12	65.5 (3)
W1—P1—C1—C6	−21.3 (3)	C13—P1—C7—C12	170.5 (3)
C7—P1—C1—C2	32.5 (3)	W1—P1—C7—C12	−62.2 (3)
C13—P1—C1—C2	−73.6 (3)	C12—C7—C8—C9	−0.5 (5)
W1—P1—C1—C2	157.9 (2)	P1—C7—C8—C9	−179.7 (3)
C6—C1—C2—C3	1.0 (5)	C7—C8—C9—C10	0.0 (5)

P1—C1—C2—C3	−178.1 (3)	C8—C9—C10—C11	−0.5 (5)
C1—C2—C3—C4	0.9 (5)	C9—C10—C11—C12	1.4 (5)
C2—C3—C4—C5	−1.7 (5)	C10—C11—C12—C7	−1.8 (5)
C3—C4—C5—C6	0.7 (5)	C8—C7—C12—C11	1.4 (5)
C2—C1—C6—C5	−2.1 (5)	P1—C7—C12—C11	−179.4 (3)
P1—C1—C6—C5	177.1 (2)	C7—P1—C13—C13^i	−172.8 (3)
C4—C5—C6—C1	1.2 (5)	C1—P1—C13—C13^i	−68.3 (3)
C1—P1—C7—C8	−115.3 (3)	W1—P1—C13—C13^i	61.0 (3)
C13—P1—C7—C8	−10.3 (3)		

Symmetry code: (i) −x, −y+1, −z+1.