Journal of Organometallic Chemistry, 366 (1989) 265–274
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09729

Iridium carbonyl clusters

VIII *. The crystal structure of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_4(\mu\text{-}CO)_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, a "60-electron" cluster with a triangulated rhomboidal W_2Ir_2 skeleton

Melvyn Rowen Churchill and Linda Vollaro Biondi

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214 (U.S.A.)

(Received October 4th, 1988)

Abstract

The reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with PhC≡CPh has previous been shown to produce, inter alia, a complex of stoichiometry $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(PhCCPh)_2$. This is shown here to be the dimetalloallyl-benzylidyne complex $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_4(\mu\text{-}CO)_2$ $(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, which crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with a 14.253(9), b 15.629(4), c 18.731(4) Å, β 96.86(4)°, V 4143(3) Å^3 and $Z = 4$. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer (Mo-K_α radiation, 2θ 4.5–45.0°). Substantial crystal decomposition was observed, but the structure was solved and refined to R 8.5% for all 4887 data (R 5.8% for those 3395 data with $|F_o| > 3\sigma(|F_o|)$).

The complex, although a "60-electron" cluster, has a triangulated rhomboidal skeleton (dihedral angle 170.33°) with W(1) and Ir(1) as the bridgehead atoms. Metal–metal distances show some irregularities and there are two "semi-bridging" carbonyl ligands, possibly as a result of the formally "electron-poor" environment of Ir(1). Metal–metal bond lengths are W(1)–W(2) 3.080(1), Ir(1)–Ir(2) 2.720(1), W(2)–Ir(1) 2.665(1), W(1)–Ir(1) 2.723(2) and W(1)–Ir(2) 2.852(2) Å. The μ_3-benzylidyne fragment is linked to W(1), W(2) and Ir(1), while the $\mu_3\text{-}\eta^3\text{-}C_3Ph_3$ ligand is σ-bonded to W(1) and Ir(1) and is π-bonded (η^3 mode) to Ir(2). The μ_3-CPh and $\mu_3\text{-}\eta^3\text{-}C_3Ph_3$ ligands lie on the same surface of the close-to-planar W_2Ir_2 cluster.

---

* For previous parts, see references 1–7.

0022-328X/89/$03.50

Introduction

The syntheses [8] and structures of $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ [4] and $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ [3] have previously been reported. These mixed-metal clusters have also been investigated as sources of bimetallic particles on alumina surfaces [8]. A few reactions of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with small organic molecules have been investigated. The reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with N_2CHCO_2Et produces the bis(alkylidene) complex $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$, a 60-electron tetrahedral cluster [1,9]. The reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with alkynes ($RC{\equiv}CR$) proceeds via two pathways [10]. The predominant reaction is cleavage of a W–W bond to form $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_8(RCCR)$. However, with $PhC{\equiv}CPh$, a second type of product is obtained of overall stoichiometry $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(PhCCPh)_2$, which we now show to be $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$. This is derived from $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ by cleavage of a W–Ir (rather than W–W) bond along with alkyne cleavage and alkyne-alkylidyne addition. A brief account of this work has appeared previously [10].

Experimental

Crystals of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, synthesized and characterized (^1H and ^{13}C NMR, IR, MS(FAB) with m/z 1406 ($M+$), $1406-28x$, $x = 1$–6) as described previously [10], were supplied to us by Professor J.R. Shapley and Dr. C.H. McAteer of the University of Illinois at Urbana-Champaign.

The crystal selected for the X-ray diffraction study was a rather irregular dark-green fragment approximating to a needle of dimensions 0.15 × 0.2 × 0.4 mm. This was sealed, in a dry, purified argon atmosphere, into a 0.2 mm-diameter thin-walled glass capillary, which was mounted on a eucentric goniometer on a Syntex $P2_1$ four-circle diffractometer. Crystal alignment, determination of Laue group ($2/m$, monoclinic system), orientation matrix and cell dimensions (based upon 24 reflections with 2θ 25–30° and well dispersed in reciprocal space) were all carried out in a manner described previously [11]. Unit cell dimensions and details of data collection appear in Table 1.

All data were corrected empirically for the effects of absorption ($\mu(\text{Mo-}K_\alpha)$ 127 cm^{-1}) by interpolation in both 2θ and ϕ between a series of normalized transmission curves based upon ψ-scans of close-to-axial reflections. It proved necessary also to correct all data for the effects of decay. Analysis of the three standard reflections showed a steady monotonic decrease of intensity throughout data collection, finishing with intensities approximately 72% of their initial values. A linear correction was made to scale up all intensity measurements. Corrections for Lorentz and polarization factors were applied and data were merged to a unique set of $|F_o|$ values. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$; none was eliminated. All data were placed upon an approximately absolute scale by means of a Wilson plot.

The systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) are consistent only with the pervasive centrosymmetric monoclinic space group $P2_1/c$ [12].

All crystallographic calculations were performed on a CDC Cyber 173 computer using the programs MULTAN76 [13] and SHELX76 [14]. The positions of the four metal atoms were determined from an "E-map." (Distinction between tungsten

Table 1

Experimental data for the X-ray diffraction study of (η^5-C_5H_5)$_2W_2Ir_2(CO)_4$(μ-CO)$_2$(μ_3-CPh)(μ_3-η^3-C_3Ph_3)

(A) Crystal parameters at 24 °C

Cryst. system:	monoclinic	Space group:	$P2_1/c$ (C_{2h}^5; No. 14)
a	14.253(9) Å	Formula:	$C_{44}H_{30}Ir_2O_6W_2$
b	15.629(4) Å	Mol. wt:	1406.7
c	18.731(4) Å	Z =	4
β	96.86(4)°	D(calcd.):	2.26 g cm^{-3}
V	4143(3) Å^3		

(B) Collection of diffraction data

Diffractometer:	Syntex $P2_1$
Radiation:	Mo-K_α (λ 0.710730 Å)
Monochromator:	Highly oriented (pyrolytic) graphite, equatorial mode, $2\theta_m$ 12.2°, assumed 50% perfect/50% ideally mosaic for polarization correction.
Scan type:	Coupled θ(crystal) − 2θ(counter) at 2.5 deg/min in 2θ.
Scan width:	Symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
Reflections measd:	$+h$, $+k$, $\pm l$ and 2θ 4.5–45.0°; 6151 total yielding 4887 unique data.
Bkgd. measurement:	Stationary crystal and counter at each end of the 2θ scan; each for one-half of total scan time.
Standard reflections:	3 approximately mutually orthogonal reflections measured after each 97 reflections; decay to 72% of initial values observed and corrected by a linear method.
Absorption coeff.:	μ(Mo-K_α) 127.0 cm^{-1}; empirical correction applied.

($Z = 74$) and iridium ($Z = 77$) atoms was not possible at this stage and was made later on the basis of chemical connectivity, based particularly upon the assumption that the η^5-C_5H_5 ligands remained associated with the tungsten atoms.) All remaining non-hydrogen atoms were located from difference-Fourier syntheses. Least-squares refinement of positional and thermal parameters (anisotropic for metal atoms, isotropic for all others) led to convergence with $R(F)$ 8.5% and $R(wF)$ 8.5% for 237 parameters refined against all 4887 data. The residuals for those 3395 data with $|F_o| > 3\sigma(|F_o|)$ were $R(F)$ 5.8% and $R(wF)$ 5.8%. (Contributions from hydrogen atoms were not included in the calculations.) These rather high values may be related to crystal decomposition. A final difference-Fourier synthesis showed no significant features other than peaks of height 1.2–1.5 e$^-$/Å^3 in the vicinity of the metal atoms' locations. Final positional and thermal parameters are collected in Table 2.

Discussion

The crystal consists of discrete ordered molecular units of (η^5-C_5H_5)$_2W_2Ir_2$-$(CO)_4$(μ-CO)$_2$(μ_3-CPh)(μ_3-η^3-C_3Ph_3), which are mutually separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. Each molecule is chiral, but the crystal contains an ordered racemic mixture of the two enantiomers by virtue of the inversion centers and c-glide planes present in the centrosymmetric monoclinic space group $P2_1/c$. The (η^5-C_5)$_2W_2Ir_2(CO)_4$(μ-CO)$_2$-(μ_3-C–C)(μ_3-η^3-C_3(*ipso*-C)$_3$) core of the molecule is shown in Fig. 1; the labelling scheme for all atoms in the molecule is shown in Fig. 2 and a stereoscopic view of

Table 2

Final positional parameters (with esd's) for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_4(\mu\text{-}CO)_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$

Atom	x	y	z	U (Å^2)
Ir(1)	0.1611(1)	0.7502(1)	0.2211(1)	
Ir(2)	0.2141(1)	0.7638(1)	0.3650(1)	
W(1)	0.0652(1)	0.8655(1)	0.2938(1)	
W(2)	0.0113(1)	0.8092(1)	0.1367(1)	
O(5)	0.2402(18)	0.5761(17)	0.1939(13)	0.1011(76)
O(6)	0.2749(18)	0.7720(17)	0.5250(14)	0.1054(78)
O(7)	0.2394(22)	0.5726(22)	0.3739(17)	0.1359(104)
O(8)	0.0111(14)	0.6804(13)	0.3448(10)	0.0696(53)
O(9)	0.0853(15)	0.6445(14)	0.0737(11)	0.0773(58)
O(10)	−0.1204(16)	0.7001(14)	0.2220(12)	0.0826(63)
C(5)	0.2094(19)	0.6488(18)	0.2023(14)	0.0560(69)
C(6)	0.2523(25)	0.7732(23)	0.4643(20)	0.0871(101)
C(7)	0.2314(38)	0.6513(38)	0.3721(29)	0.1460(183)
C(8)	0.0555(16)	0.7465(15)	0.3337(12)	0.0426(55)
C(9)	0.0736(19)	0.7061(18)	0.1103(14)	0.0577(68)
C(10)	−0.0644(19)	0.7420(18)	0.1908(14)	0.0597(69)
C(1)	0.2127(17)	0.9025(16)	0.3360(13)	0.0493(62)
C(11)	0.2201(18)	0.9750(17)	0.3919(14)	0.0546(66)
C(12)	0.2017(19)	0.9632(17)	0.4633(14)	0.0555(68)
C(13)	0.2179(21)	1.0378(20)	0.5101(16)	0.0677(81)
C(14)	0.2515(20)	1.1113(19)	0.4880(15)	0.0647(75)
C(15)	0.2747(18)	1.1206(17)	0.4167(14)	0.0530(66)
C(16)	0.2643(17)	1.0524(16)	0.3678(13)	0.0463(59)
C(2)	0.2935(17)	0.8705(16)	0.3130(13)	0.0444(59)
C(21)	0.3857(21)	0.9096(19)	0.3309(16)	0.0654(77)
C(22)	0.4293(24)	0.9086(22)	0.4010(18)	0.0765(92)
C(23)	0.5207(25)	0.9423(24)	0.4196(19)	0.0904(103)
C(24)	0.5678(30)	0.9864(28)	0.3653(23)	0.1097(129)
C(25)	0.5248(28)	0.9865(25)	0.2938(21)	0.0965(114)
C(26)	0.4331(21)	0.9512(19)	0.2781(16)	0.0654(78)
C(3)	0.1140(20)	0.8811(18)	0.1982(15)	0.0612(72)
C(31)	0.1740(18)	0.9440(17)	0.1645(14)	0.0531(67)
C(32)	0.2287(18)	0.9197(17)	0.1135(14)	0.0553(66)
C(33)	0.2807(23)	0.9820(21)	0.0795(17)	0.0742(90)
C(34)	0.2726(21)	1.0711(20)	0.0944(16)	0.0686(81)
C(35)	0.2141(24)	1.0927(22)	0.1467(18)	0.0839(94)
C(36)	0.1692(18)	1.0313(16)	0.1828(13)	0.0492(63)
C(4)	0.2920(18)	0.7930(16)	0.2670(13)	0.0537(64)
C(41)	0.3824(19)	0.7532(18)	0.2554(15)	0.0609(71)
C(42)	0.4428(26)	0.7202(23)	0.3076(19)	0.0894(103)
C(43)	0.5311(31)	0.6917(28)	0.2933(23)	0.1088(131)
C(44)	0.5587(32)	0.6942(30)	0.2210(25)	0.1168(142)
C(45)	0.4913(31)	0.7228(27)	0.1670(22)	0.1111(127)
C(46)	0.3986(29)	0.7552(27)	0.1801(22)	0.1080(121)
Cp(1)	0.0199(21)	0.9985(20)	0.3424(16)	0.0703(80)
Cp(2)	−0.0072(21)	0.9287(19)	0.3886(16)	0.0673(78)
Cp(3)	−0.0806(23)	0.8818(21)	0.3509(17)	0.0773(90)
Cp(4)	−0.0918(24)	0.9150(22)	0.2777(18)	0.0770(92)
Cp(5)	−0.0357(21)	0.9874(19)	0.2775(16)	0.0665(79)
Cp(6)	−0.0338(26)	0.9371(24)	0.0729(20)	0.0923(105)
Cp(7)	0.0088(28)	0.8835(26)	0.0258(21)	0.1012(115)
Cp(8)	−0.0525(26)	0.8111(24)	0.0163(19)	0.0888(103)
Cp(9)	−0.1234(28)	0.8157(26)	0.0527(21)	0.0980(113)
Cp(10)	−0.1203(29)	0.8927(27)	0.0908(22)	0.1084(124)

Table 2 (continued)
Anisotropic thermal parameters (with esd's) for the metal atoms [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	0.0922(8)	0.0336(5)	0.0320(5)	−0.0004(4)	0.0076(5)	0.0016(5)
Ir(2)	0.0927(9)	0.0432(6)	0.0326(5)	0.0086(5)	0.0070(5)	0.0024(6)
W(1)	0.0824(8)	0.0402(6)	0.0278(5)	0.0004(4)	0.0081(5)	0.0022(6)
W(2)	0.0985(9)	0.0423(6)	0.0271(5)	0.0031(5)	0.0026(5)	−0.0052(6)

[a] These values are in standard SHELX76 format.

the molecule appears as Fig. 3. Intramolecular distances and angles are provided in Tables 3 and 4.

Interestingly, the reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with two moles of PhC≡CPh is shown to give rise to a product in which the two alkyne ligands have undergone reorganization to produce a μ_3-CPh ligand (formally a 3-electron donor) and a $\mu_3\text{-}\eta^3\text{-}C_3Ph_3$ ligand (formally a 5-electron donor). These two fragments lie on the same surface of a triangulated rhomboidal W_2Ir_2 cluster. The metal atom core is close to planar with a dihedral angle of 170.33° between the W(1)–Ir(1)–Ir(2) and W(1)–W(2)–Ir(1) triangles.

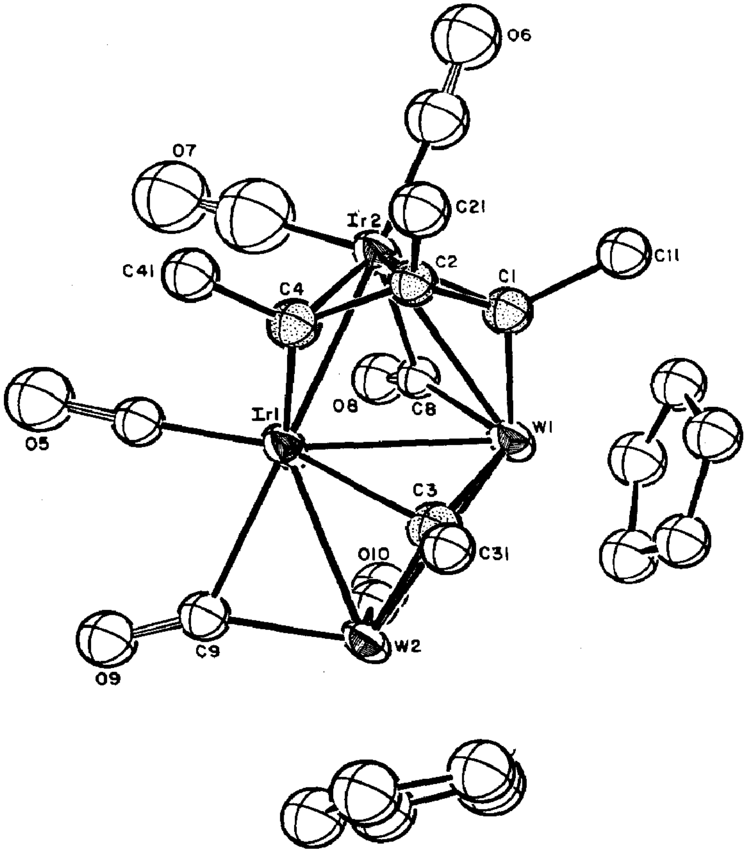

Fig. 1. The $(\eta^5\text{-}C_5)_2W_2Ir_2(CO)_4(\mu\text{-}CO)_2(\mu_3\text{-}C\text{-}C)(\mu_3\text{-}\eta^3\text{-}C_3(\textit{ipso}\text{-}C)_3$ core of the molecule.

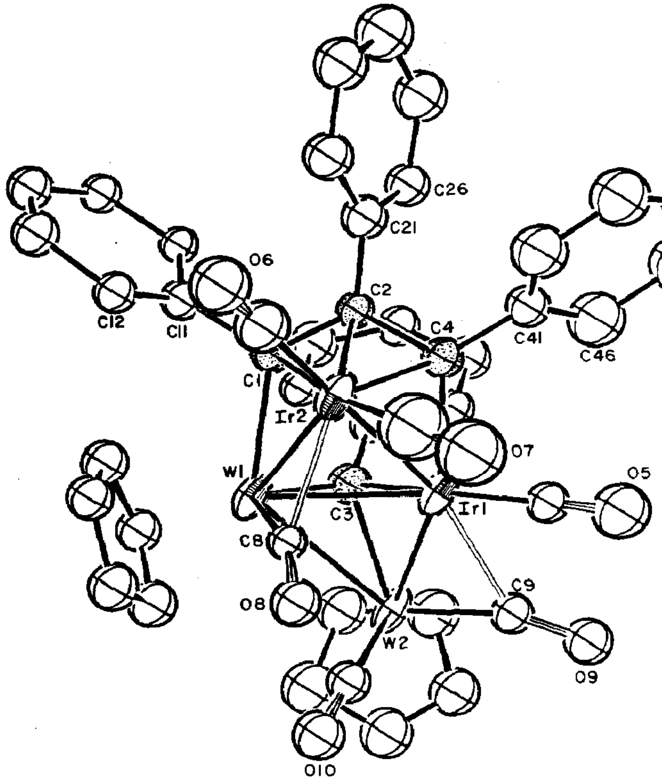

Fig. 2. Labelling of atoms in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_4(\mu\text{-}CO)_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ molecule. Hydrogen atoms are omitted.

Planar triangulated rhomboidal clusters and the electronically equivalent "butterfly" clusters are usually associated with 62 outer valence electrons whereas tetrahedral clusters typically have 60 outer valence electrons. The present close-to-

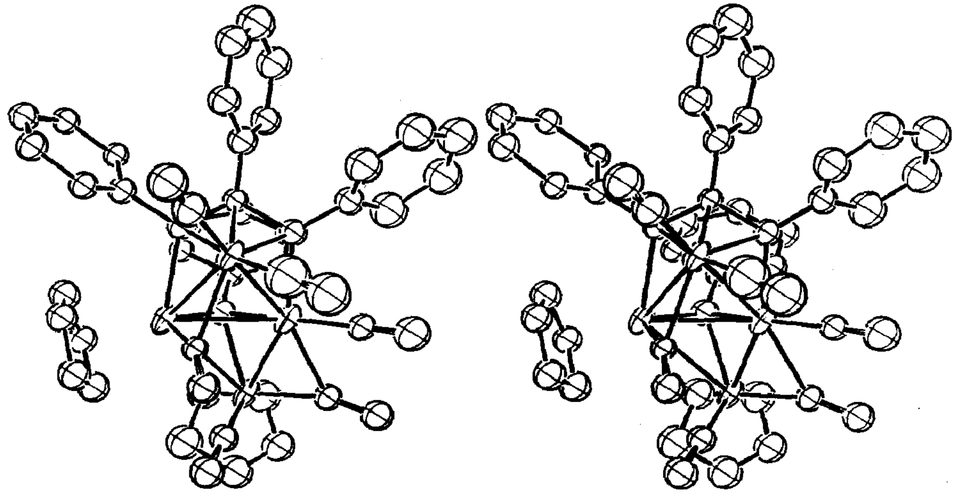

Fig. 3. A stereoscopic view of the molecule.

Table 3

Interatomic distances (Å), with esd's, for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_4(\eta\text{-}CO)_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$

Atoms	Distance	Atoms	Distance
(A) Metal – Metal distances			
W(1)–W(2)	3.080(1)	Ir(1)–Ir(2)	2.720(1)
W(1)–Ir(1)	2.723(2)	W(2)–Ir(1)	2.665(2)
W(1)–Ir(2)	2.852(2)		
(B) Metal – η^3*-*C_3Ph_3 *distances*			
Ir(2)–C(1)	2.233(25)	W(1)–C(1)	2.231(24)
Ir(2)–C(4)	2.302(26)	Ir(1)–C(4)	2.069(24)
Ir(2)–C(2)	2.296(25)		
(C) Metal – μ_3*-CPh distances*			
W(1)–C(3)	2.012(29)	Ir(1)–C(3)	2.180(28)
W(2)–C(3)	2.081(27)		
(D) Selected of distances within the μ_3*-*η^3*-*C_3Ph_3 *ligand*			
C(1)–C(11)	1.539(36)	C(1)–C(2)	1.370(36)
C(2)–C(21)	1.452(37)	C(2)–C(4)	1.486(35)
C(4)–C(41)	1.470(38)		
(E) Distances within the μ_3*-CPh ligand*			
C(3)–C(31)	1.492(40)	C(34)–C(35)	1.401(48)
C(31)–C(32)	1.356(39)	C(35)–C(36)	1.376(44)
C(32)–C(33)	1.420(43)	C(36)–C(31)	1.411(37)
C(33)–C(34)	1.428(45)		
(F) Metal – carbon (carbonyl) distances			
Ir(1)–C(5)	1.780(28)	W(1)–C(8)	2.016(23)
Ir(2)–C(6)	1.880(36)	Ir(2) · · · C(8)	2.282(22)
Ir(2)–C(7)	1.778(58)	W(2)–C(9)	1.932(28)
W(2)–C(10)	1.886(28)	Ir(1) · · · C(9)	2.391(25)
(G) Carbon – oxygen (carbonyl) distances			
C(5)–O(5)	1.235(38)	C(8)–O(8)	1.242(31)
C(6)–O(6)	1.144(44)	C(9)–O(9)	1.205(35)
C(7)–O(7)	1.236(68)	C(10)–O(10)	1.232(36)
(H) Metal – η^5*-*C_5H_5 *ligand distances*			
W(1)–Cp(1)	2.389(31)	W(2)–Cp(6)	2.377(37)
W(1)–Cp(2)	2.373(31)	W(2)–Cp(7)	2.376(39)
W(1)–Cp(3)	2.461(34)	W(2)–Cp(8)	2.328(35)
W(1)–Cp(4)	2.354(33)	W(2)–Cp(9)	2.335(37)
W(1)–Cp(5)	2.384(30)	W(2)–Cp(10)	2.362(41)
W(1)–Cp [a]	2.066	W(2)–Cp [a]	2.032

[a] Cp is the centroid of the appropriate η^5-C_5H_5 ligand

planar triangulated rhomboidal cluster has a total of only 60 outer valence electrons. (With a neutral atom, neutral ligand counting system we have two d^6 W(0) atoms, two d^9 Ir(0) atoms, 12e$^-$ from the six carbonyl ligands, 10e$^-$ from the two η^5-C_5H_5 ligands, 5e$^-$ from the μ_3–η_3-C_3Ph_3 ligand and 3e$^-$ from the μ_3-CPh ligand.) Electron counts for the individual metal atoms (with electrons of the two "semi-bridging" carbonyl ligands associated formally with the most tightly bound metal atom) are 18e$^-$ at W(1), W(2) and Ir(2) and 16e$^-$ at Ir(1).

Table 4

Selected interatomic angles (deg) for $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_3\text{-CPh})(\mu_3\text{-}\eta^3\text{-C}_3\text{Ph}_3)$

Atoms	Angle	Atoms	Angle
(A) Intermetallic angles			
W(1)–Ir(1)–Ir(2)	63.2(0)	Ir(2)–W(1)–Ir(1)	58.4(0)
W(2)–Ir(1)–Ir(2)	132.0(1)	W(2)–W(1)–Ir(1)	54.2(0)
W(2)–Ir(1)–W(1)	69.7(0)	W(2)–W(1)–Ir(2)	112.0(0)
W(1)–Ir(2)–Ir(1)	58.5(0)	W(1)–W(2)–Ir(1)	56.0(0)
(B) Metal–metal–carbon angles involving the (μ_3-η^3-C_3Ph_3) and (μ_3-CPh) ligands			
Ir(1)–Ir(2)–C(1)	80.9(6)	W(1)–Ir(2)–C(1)	50.3(6)
Ir(1)–Ir(2)–C(2)	74.3(6)	W(1)–Ir(2)–C(4)	85.4(6)
Ir(1)–Ir(2)–C(4)	47.8(6)	W(1)–Ir(1)–C(3)	46.9(8)
Ir(1)–W(1)–C(1)	80.8(7)	W(1)–Ir(1)–C(4)	93.4(7)
Ir(1)–W(1)–C(3)	52.2(8)	W(1)–W(2)–C(3)	40.4(8)
Ir(1)–W(2)–C(3)	53.0(8)	W(2)–Ir(1)–C(3)	49.6(7)
Ir(2)–W(1)–C(1)	50.3(6)	W(2)–Ir(1)–C(4)	138.9(7)
Ir(2)–W(1)–C(3)	99.6(8)	W(2)–W(1)–C(1)	122.0(6)
Ir(2)–Ir(1)–C(3)	99.5(7)	W(2)–W(1)–C(3)	42.0(8)
Ir(2)–Ir(1)–C(4)	55.5(7)		
(C) Metal–carbon–oxygen angles			
Ir(1)–C(5)–O(5)	175.2(25)	W(1)–C(8)–O(8)	152.6(18)
Ir(2)–C(6)–O(6)	174.6(32)	Ir(2) ··· C(8)–O(8)	124.4(17)
Ir(2)–C(7)–O(7)	176.5(42)	W(2)–C(9)–O(9)	155.6(21)
W(2)–C(10)–O(10)	174.4(22)	Ir(1) ··· C(9)–O(9)	129.1(19)
(D) M–C–C angles involving the (μ_3-η^3-C_3Ph_3) and (μ_3-CPh) ligands			
Ir(1)–C(3)–C(31)	121.5(19)	Ir(1)–C(4)–C(2)	117.0(17)
Ir(1)–C(4)–C(41)	124.4(18)	Ir(2)–C(1)–C(2)	74.9(15)
Ir(2)–C(1)–C(11)	123.5(17)	Ir(2)–C(2)–C(1)	69.9(15)
Ir(2)–C(2)–C(21)	133.3(18)	Ir(2)–C(2)–C(4)	71.4(14)
Ir(2)–C(4)–C(41)	123.2(18)	Ir(2)–C(4)–C(2)	70.9(14)
W(1)–C(1)–C(11)	114.6(17)	W(1)–C(1)–C(2)	125.9(18)
W(1)–C(3)–C(31)	137.2(20)		
W(2)–C(3)–C(31)	121.5(18)		

Metal-metal bond lengths in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_3\text{-CPh})(\mu_3\text{-}\eta^3\text{-C}_3\text{Ph}_3)$ may be compared to those in the isonuclear tetrahedral clusters $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$ (**A**) [3,8] and $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_7(\text{CHCO}_2\text{Et})_2$ (**B**) [1,9]. Thus, the W(1)–W(2) bond length of 3.080(1)Å is significantly longer than W–W 2.991(1) Å in **A** and 2.995(1) Å in **B**. The Ir(1)–Ir(2) bond length of 2.720(1) is similar to that of 2.722(1) Å in **A**; both are longer than the value of 2.653(1) Å in **B**. Tungsten–iridium distances in the present complex are, in increasing order, W(2)–Ir(1) 2.665(2) Å, W(1)–Ir(1) 2.723(2) Å and W(1)–Ir(2) 2.852(2) Å. Those in **A** range from 2.796(1) through 2.863(1) Å; those in **B** lie in the range 2.781(1)–2.825(1) Å. The anomalous feature appears to be that the two W–Ir distances involving the formally electron-poor atom Ir(1) in the present structure are shorter than in all other cases.

Each metal atom is in a different chemical environment from the others. Atom W(1) is linked to the three other metal atoms, an η^5-C_5H_5 ligand, via a σ-bond to C(1) of the μ_3-η^3-C_3Ph_3 ligand, to C(3) of the μ_3-CPh ligand and to the carbonyl ligand C(8)–O(8) (which also interacts more weakly with Ir(2)). Atom W(2) is linked to two metal atoms (W(1) and Ir(1)), an η^5-C_5H_5 ligand, to C(3) of the μ_3-CPh ligand and two carbonyl ligands, C(10)–O(10) and C(9)–O(9) (the latter of which also interacts weakly with Ir(1)). Atom Ir(1) is linked to the three metal atoms, via a σ-bond to C(4) of the μ_3-η^3-C_3Ph_3 ligand, to C(3) of the μ_3-CPh ligand and to the carbonyl ligand C(5)–O(5). Atom Ir(2) is linked to two metal atoms (W(1) and Ir(1)), is linked via an η^3-linkage to the allylic system C(1)–C(2)–C(4) in the μ_3-η^3-C_3Ph ligand and to two terminal carbonyl ligands, C(6)–O(6) and C(7)–O(7).

The μ_3-η^3-C_3Ph_3 system participates in a dimetalloallyl system. It is σ-bonded to W(1) and Ir(1) with W(1)–C(1) 2.231(24) Å and Ir(1)–C(4) 2.069(24) Å and it is is π-bonded to Ir(2) with Ir(2)–C(1) 2.233(25), Ir(2)–C(2) 2.296(25) and Ir(2)–C(4) 2.302(26) Å.

The μ_3-CPh (benzylidyne) ligand forms σ-bonds to three metal atoms with W(1)–C(3) 2.012(29), W(2)–C(3) 2.081(27) and Ir(1)–C(3) 2.180(28) Å. The μ_3-η^3-C_3Ph_3 and μ_3-CPh ligands lie on the same surface of the rhomboidal W_2Ir_2 cluster; it is possibly the interaction between these systems that causes the slight non-planarity of the metal core.

Four of the carbonyl ligands are clearly terminal and are close to colinear with the metal atom viz. Ir(1)–C(5) 1.780(28) Å with angle Ir(1)–C(5)–O(5) 175.2(25)°, Ir(2)–C(6) 1.880(36) Å with angle Ir(2)–C(6)–O(6) 174.6(32)°, Ir(2)–C(7) 1.778(58) Å with Ir(2)–C(7)–O(7) 176.5(42)°, and W(2)–C(10) 1.886(28) Å with angle W(2)–C(10)–O(10) 174.4(22)°. The remaining two are clearly in "semi-bridging" positions. The ligand C(8)–O(8) is associated with metal–carbon distances of W(1)–C(8) 2.016(23) Å and Ir(2) $\cdots$ C(8) 2.282(22) Å and with the angles W(1)–C(8)–O(8) 152.6(18)° and Ir(2) $\cdots$ C(8)-O(8) 124.4(17)°. This system is associated with an α-value (defined by $(d_2 - d_1)/d_1$ [15] of 0.13 and a "partially-corrected α-value" [1], defined by $[(d_1 - r(M_1)) - (d_2 - r(M_2))]/d_1$ of 0.22. The latter value, based on internal radii of r(W) 1.54 Å and r(Ir) 1.36 Å, is more useful and confirms the semi-bridging rather than symmetrically bridging nature of this system.

The ligand C(9)–O(9) has W(2)–C(9) 1.932(28) Å, Ir(1) $\cdots$ C(9) 2.391(25) Å, < W(2)–C(9)–O(9) 155.6(21)°, and Ir(1) $\cdots$ C(9)–O(9) 129.1(19)°; this system is associated with an α-value of 0.24 and a "partially-corrected α-value" of 0.33.

While it can be claimed that the second system allows electrons to be transferred to the electron-poor atom Ir(1), there is no clear electronic rationale for the existence of the first, more symmetrical, semi-bridging carbonyl.

The most interesting feature of the molecule is that it is an anomalous "60-electron" triangulated rhomboidal cluster. (This is probably due to steric effects; the μ_3-CPh and μ_3-η^3-C_3Ph_3 ligands contribute a total of only eight electrons, yet effectively block one entire surface of the W_2Ir_2 cluster; potential axial sites for a carbonyl ligand on Ir(1) are blocked by phenyl rings on one side and by C(7)–O(7) on the other side.) This phenomenon is not unique; the complex $Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}$ [16] also is rhomboidal with only 60 electrons. Also, a number of "64-electron" clusters are known which incorporate a planar trangulated rhomboidal skeleton. The simplest of these is probably $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$ [17]. The anomalous species usually exhibit expanded or contracted M–M bonds in distinct contrast to the regular geometry observed in such archetypal "62-electron" planar triangulated rhomboidal species as $Re_4(CO)_{16}{}^{2-}$ [18,19] and $HOs_3Re(CO)_{15}$ [20].

Additional material

A table of observed and calculated structure factor amplitudes is available upon request (from M.R.C.).

References

1 Part VII. M.R. Churchill and L.V. Biondi, J. Organomet. Chem., 353 (1988) 73.
2 Part VI. M.R. Churchill, Y.-J. Li, J.R. Shapley, D.S. Foose and W.S. Uchiyama, J. Organomet. Chem., 312 (1986) 121.
3 Part V. M.R. Churchill, C. Bueno and J.P. Hutchinson, Inorg. Chem., 21 (1982) 1359.
4 Part IV. M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 20 (1981) 4112.
5 Part III. M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 19 (1980) 2765.
6 Part II. M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 18 (1979) 2451.
7 Part I. M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 17 (1978) 3528.
8 J.R. Shapley, S.J. Hardwick, D.S. Foose, G.D. Stucky, M.R. Churchill, C. Bueno and J.P. Hutchinson, J. Am. Chem. Soc., 103 (1981) 7383.
9 M.R. Churchill, L.V. Biondi, J.R. Shapley and C.H. McAteer, J. Organomet. Chem., 280 (1985) C63.
10 J.R. Shapley, C.H. McAteer, M.R. Churchill and L.V. Biondi, Organometallics, 3 (1984) 1595.
11 M.R. Churchill, R.A. Lashewycz and F.J. Rotella, Inorg. Chem., 16 (1977) 265.
12 International Tables for X-Ray Crystallography, Volume 1, p. 99; Kynoch Press, Birmingham, England, 1965.
13 G. Germain, P. Main and M.M. Woolfson, Acta Crystallogr., A, 27 (1971) 368.
14 G.M. Sheldrick, SHELX, Cambridge, 1976.
15 M.D. Curtis, K.R. Han and W.M. Butler, Inorg. Chem., 19 (1980) 2096.
16 L.J. Farrugia, J.A.K. Howard, P. Mitrprachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 171.
17 M.R. Churchill, C. Bueno and D.A. Young, J. Organomet. Chem., 213 (1981) 139.
18 R. Bau, B. Fontal, H.D. Kaesz and M.R. Churchill, J. Am. Chem. Soc., 89 (1967) 6374.
19 M.R. Churchill and R. Bau, Inorg. Chem., 7 (1968) 2606.
20 M.R. Churchill and F.J. Hollander, Inorg. Chem., 16 (1977) 2493.