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# Iridium carbonyl clusters

## VII *. The crystal structure of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$, a tetrahedral cluster with a simple bridging and a triply-bridging alkylidene-ester ligand

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### Abstract

The reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with $N_2CHCO_2Et$ produces the bis(alkylidene) species $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ which has been subjected to an X-ray structural analysis. The complex $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ crystallizes in the centrosymmetric monoclinic space group $C2/c$ (No. 15) with $a$ 34.097(5), $b$ 8.7057(12), $c$ 19.811(3) Å, $\beta$ 111.053(12)°, $V$ 5488 Å$^3$ and $Z = 8$. Diffraction data were collected with a Syntex P$2_1$ automated diffractometer (Mo-$K_\alpha$ radiation, $2\theta$ 4.5–45.0°) and the structure was solved and refined to $R$ 4.7% for all 3621 independent data ($R$ 3.9% for those 3216 data with $|F_o| > 3\sigma(|F_o|)$).

$(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ contains a tetrahedral cluster of metal atoms. Ir(1) and Ir(2) are each associated with two terminal carbonyl ligands and are bridged by a $>$CHCO$_2$Et ligand. Each tungsten atom is linked to an $\eta^5$-$C_5H_5$ ligand; W(1) is associated with only one carbonyl ligand, whereas W(2) is associated with two (one of which is involved in a "semi-bridging" interaction with Ir(2)). The structure is completed by a second CHCO$_2$Et ligand; the alkylidene carbon atom bridges Ir(1) and W(2) while the ketonic oxygen forms a donor bond to W(1).

### Introduction

The syntheses [7] and structures of the mixed metal clusters $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ [3] and $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ [2] have previously been reported along with studies as their utility as precursors to alumina-supported bimetallic particles [7]. It is of

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* For previous parts, see ref. 1–6.

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interest to ascertain how these bimetallic clusters behave in their reactions with small organic moieties. We have shown previously [8] that the tetrahedral heterometallic cluster $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ reacts with alkynes ($RC\equiv CR$) by two pathways involving: (i) cleavage of a W–W bond to form $(\eta^5\text{-}C_5H_5)_2Ir_2W_2(CO)_8(C_2R_2)$, a species in which the $W_2Ir_2C_2$ framework is octahedral, and (ii) cleavage of an Ir–Ir bond along with ligand cleavage and alkylidene-alkyne coupling to form the $\mu_3$-alkylidyne-$\mu_3$-$\eta^3$-allyldiyl species $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CR)(\mu_3\text{-}\eta^3\text{-}C_3R_3)$. We now report a structural study of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$, produced by reaction of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ with ethyl diazoacetate, $N_2CHCO_2Et$. A preliminary account of this work has been published previously [9].

## Experimental

Crystals suitable for X-ray diffraction studies, synthesized and characterized as described previously [9], were supplied by Professor J.R. Shapley and Dr. C.H. McAteer of the University of Illinois.

A purple-brown, rather plate-like, crystal of approximate orthogonal dimensions 0.3 × 0.2 × 0.1 $mm^3$ was selected for the X-ray diffraction study. It was sealed, in an inert (Ar) atmosphere, into a 0.2 mm-diameter thin-walled glass capillary, which was mounted on a eucentric goniometer on a Syntex $P2_1$ automated four-circle diffractometer. Crystal alignment, determination of crystal class (monoclinic, $2/m$ diffraction symmetry), the orientation matrix and accurate cell dimensions (based on 25 reflections with $2\theta$ 25–30°, appropriately dispersed in reciprocal space) were carried out as has been described previously [10]. Details of data collection (using a coupled $\theta$(crystal)–$2\theta$(counter) scan) are given in Table 1.

All data were corrected empirically for the effects of absorption ($\mu$ 191.6 $cm^{-1}$) by interpolation, in both $2\theta$ and $\phi$, between normalized transmission curves based upon $\psi$-scans of a series of close-to-axial reflections. Corrections for Lorentz and polarization factors were applied and data were merged to provide a unique set. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$; none was expunged. Data were placed upon an approximately absolute scale by means of a Wilson plot.

The diffraction symmetry ($C_{2h}$; $2/m$) and the systematic absences $hkl$ for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ ($h = 2n + 1$) are consistent with the noncentrosymmetric space group $Cc$ ($C_s^4$; No. 9) or the centrosymmetric monoclinic space group $C2/c$ ($C_{2h}^6$; No. 15) [11]. The latter centrosymmetric possibility was chosen on the basis of (a) intensity statistics and (b) its greater probability with $Z = 8$; the successful solution of the structure in this higher symmetry space group confirms the correctness of our choice.

## Solution and refinement of the structure

All calculations were carried out under the SUNY-Buffalo version of the Syntex XTL crystallographic program package [12]. Structure factors were based upon the analytical functions for neutral atoms [13a]; both the real ($\Delta f'$) and imaginary ($i\,\Delta f''$) components of anomalous dispersion [13b] were included for all non-hydrogen atoms. The function minimized during full-matrix least-squares refinement was

Table 1

Experimental data for the X-ray diffraction study of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$

| | |
|---|---|
| *(A) Crystal parameters at 24 °C* | |
| Cryst. system: monoclinic | Space group $C2/c$ ($C_{2h}^6$; No. 15) |
| $a$ 34.0974(52) Å | Formula $C_{25}H_{22}Ir_2O_{11}W_2$ |
| $b$ 8.7057(12) Å | Mol. wt. 1250.6 |
| $c$ 19.8106(31) Å | $Z = 8$ |
| $\beta$ 111.053(12)° | $D$(calcd.) 3.30 g cm$^{-3}$ |
| $V$ 5488.1(15) Å$^3$ | |
| *(B) Collection of diffraction data* | |
| Diffractometer | Syntex P2$_1$ |
| Radiation | Mo-$K_\alpha$ ($\bar{\lambda}$ 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 $\theta$(crystal)–$2\theta$(counter) at 2.5 deg/min in $2\theta$. |
| Scan width | symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]$° |
| Reflections measd. | $+h$, $+k$, $\pm l$ for $h + k = 2n$ and $2\theta = 4.5$–$45.0$°; 4114 total yielding 3621 unique data. |
| Bkgd measurement | stationary crystal and counter at each end of the $2\theta$ scan; each for one-half of total scan time. |
| Standard reflections | 3 approximately mutually orthogonal reflections remeasured after each 97 data reflections; no significant fluctuations nor decay were observed. |
| Absorption coeff. | $\mu$(Mo-$K_\alpha$) 191.6 cm$^{-1}$; empirical correction applied. |

$\Sigma w(|F_o| - |F_c|)^2$ where $w = [\{\sigma(|F_o|)\}^2 + \{0.03|F_o|\}^2]^{-1}$. Discrepancy indices used below are defined in eq. 1–3.

$$R_F(\%) = 100\Sigma||F_o| - F_o| - |F_c||/\Sigma|F_o| \qquad (1)$$

$$R_{wF}(\%) = 100\left[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\right]^{1/2} \qquad (2)$$

$$\mathrm{GOF} = \left[\Sigma w(|F_o| - |F_c|)^2/(NR - NP)\right]^{1/2} \qquad (3)$$

In, eq. 3, $NR$ is the number of reflections and $NP$ is the number of parameters refined.

The phase problem was solved by direct methods by use of the program MULTAN [14]; the positions of the four heavy atoms were determined from an "$E$-map". The identities of the atoms were not immediately apparent (since $Z(W) = 74$ versus $Z(Ir) = 77$) but were, in fact, assigned correctly based upon distances being W–W > W–Ir > Ir–Ir. A difference-Fourier map, based upon data phased by these four metal atoms, quickly revealed the positions of all remaining non-hydrogen atoms (and confirmed the identity of the W atoms by virtue of their attached $\eta^5$-$C_5H_5$ ligands). Least-squares refinement of positional and thermal parameters (anisotropic only for the $W_2Ir_2$ core) for all non-hydrogen atoms, with all hydrogen atoms included in idealized positions ($d$(C–H) 0.95 Å [15] and the appropriate externally-bisecting planar ($sp^2$) or staggered tetrahedral ($sp^3$) geometry) led quickly to convergence with $R_F$ 4.7%, $R_{wF}$ 5.4% and GOF = 1.30 for 181 parameters refined against all 3621 independent reflections. ($R_F$ 3.9% and $R_{wF}$ 5.0% for those

Table 2

Final positional and thermal parameters for atoms in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ molecule. Anisotropic thermal parameters (with esd's) for the metal atoms in $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$.

| Atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| Ir(1) | 0.13084(2) | 0.34064(6) | 0.01421(3) | |
| Ir(2) | 0.16282(2) | 0.62015(7) | 0.01953(3) | |
| W(1) | 0.07577(2) | 0.59219(7) | −0.03703(3) | |
| W(2) | 0.13075(2) | 0.47482(8) | −0.11440(3) | |
| O(1) | 0.03378(27) | 0.4121(11) | −0.0947(5) | 2.24(18) |
| O(2) | 0.02491(28) | 0.1828(11) | −0.1475(6) | 2.50(18) |
| O(3) | 0.22448(33) | 0.5143(14) | 0.2105(7) | 3.95(24) |
| O(4) | 0.23186(35) | 0.3281(14) | 0.1370(7) | 4.16(24) |
| O(9) | 0.07520(30) | 0.5028(12) | 0.1135(6) | 3.13(20) |
| O(10) | 0.13626(34) | 0.8383(14) | −0.1186(7) | 4.07(24) |
| O(11) | 0.0466(4) | 0.5773(15) | −0.2307(8) | 4.84(28) |
| O(12) | 0.0864(4) | 0.1459(16) | 0.0927(8) | 5.22(29) |
| O(13) | 0.1971(4) | 0.1049(15) | 0.0149(8) | 4.95(28) |
| O(14) | 0.2569(4) | 0.6060(15) | 0.0450(8) | 4.93(28) |
| O(15) | 0.1555(5) | 0.9037(18) | 0.0985(9) | 6.19(34) |
| C(1) | 0.0945(4) | 0.2820(16) | −0.0957(8) | 2.15(26) |
| C(2) | 0.0505(4) | 0.2951(18) | −0.1110(9) | 2.74(28) |
| C(3) | −0.0202(5) | 0.2080(21) | −0.1708(10) | 3.86(35) |
| C(4) | −0.0435(5) | 0.0636(19) | −0.1989(10) | 3.39(32) |
| C(5) | 0.1675(4) | 0.4695(16) | 0.1055(8) | 2.14(25) |
| C(6) | 0.2100(5) | 0.4285(19) | 0.1505(10) | 3.16(31) |
| C(7) | 0.2673(5) | 0.4948(21) | 0.2609(10) | 3.68(33) |
| C(8) | 0.2962(6) | 0.5758(26) | 0.2397(13) | 5.6(5) |
| C(9) | 0.0781(4) | 0.5232(16) | 0.0574(8) | 2.04(25) |
| C(10) | 0.1371(4) | 0.7081(18) | −0.0981(9) | 2.78(29) |
| C(11) | 0.0776(5) | 0.5415(18) | −0.1823(10) | 3.04(30) |
| C(12) | 0.1028(5) | 0.2211(19) | 0.0604(9) | 3.23(31) |
| C(13) | 0.1738(5) | 0.1995(21) | 0.0186(10) | 3.76(34) |
| C(14) | 0.2211(5) | 0.6116(18) | 0.0358(9) | 2.86(30) |
| C(15) | 0.1605(5) | 0.7965(21) | 0.0683(11) | 3.87(34) |
| Cp(1) | 0.0449(5) | 0.8023(19) | −0.1137(9) | 3.06(30) |
| Cp(2) | 0.0724(5) | 0.8597(19) | −0.0451(10) | 3.25(32) |
| Cp(3) | 0.0555(5) | 0.8075(19) | 0.0070(10) | 3.21(30) |
| Cp(4) | 0.0184(4) | 0.7162(17) | −0.0299(9) | 2.59(27) |
| Cp(5) | 0.0131(5) | 0.7192(20) | −0.1033(10) | 3.79(34) |
| Cp(6) | 0.1647(6) | 0.2757(23) | −0.1562(11) | 4.6(4) |
| Cp(7) | 0.1972(6) | 0.3752(23) | −0.1092(12) | 4.6(4) |
| Cp(8) | 0.1906(5) | 0.5126(21) | −0.1404(11) | 3.94(35) |
| Cp(9) | 0.1563(6) | 0.5173(24) | −0.2074(12) | 5.0(4) |
| Cp(10) | 0.1390(5) | 0.3695(21) | −0.2165(11) | 4.0(4) |
| H(1) | 0.0480 | 0.8187 | −0.1589 | 6.0 |
| H(2) | 0.0969 | 0.9203 | −0.0362 | 6.0 |
| H(3) | 0.0666 | 0.8288 | 0.0574 | 6.0 |
| H(4) | 0.0011 | 0.6646 | −0.0085 | 6.0 |
| H(5) | −0.0093 | 0.6708 | −0.1407 | 6.0 |
| H(6) | 0.1608 | 0.1695 | −0.1488 | 6.0 |
| H(7) | 0.2188 | 0.3476 | −0.0650 | 6.0 |
| H(8) | 0.2073 | 0.6000 | −0.1198 | 6.0 |
| H(9) | 0.1469 | 0.6026 | −0.2391 | 6.0 |
| H(10) | 0.1147 | 0.3363 | −0.2554 | 6.0 |
| H(11) | 0.0926 | 0.2140 | −0.1343 | 6.0 |

Table 2 (continued)

| Atom | $x$ | $y$ | $z$ | $B_{\text{iso}}$ |
|---|---|---|---|---|
| H(12) | 0.1597 | 0.4833 | 0.1466 | 6.0 |
| H(3A) | −0.0268 | 0.2430 | −0.1307 | 6.0 |
| H(3B) | −0.0281 | 0.2835 | −0.2078 | 6.0 |
| H(4A) | −0.0728 | 0.0824 | −0.2138 | 6.0 |
| H(4B) | −0.0356 | −0.0121 | −0.1619 | 6.0 |
| H(4C) | −0.0369 | 0.0284 | −0.2390 | 6.0 |
| H(7A) | 0.2689 | 0.5305 | 0.3071 | 6.0 |
| H(7B) | 0.2742 | 0.3887 | 0.2637 | 6.0 |
| H(8A) | 0.3236 | 0.5599 | 0.2739 | 6.0 |
| H(8B) | 0.2895 | 0.6821 | 0.2369 | 6.0 |
| H(8C) | 0.2948 | 0.5403 | 0.1935 | 6.0 |

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 1.635(24) | 2.118(28) | 1.765(29) | 0.110(18) | 0.389(20) | 0.038(21) |
| Ir(2) | 1.753(25) | 2.496(28) | 1.541(28) | −0.271(18) | 0.215(20) | 0.109(22) |
| W(1) | 1.583(24) | 2.112(28) | 1.389(28) | 0.111(18) | 0.274(20) | −0.058(21) |
| W(2) | 1.831(25) | 3.619(33) | 1.349(29) | −0.259(20) | 0.624(20) | −0.250(24) |

3216 reflections with $|F_o| > 3\sigma(|F_o|)$. A final difference-Fourier map showed no unexpected features; the largest residuals were peaks of height $\sim 1.3e^-$ in the vicinity of the metal atoms. Final positional and thermal parameters are collected in Table 2.

## Description of the structure

The crystal contains discrete molecular units of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ which are mutually separated by normal Van der Waals' distances; there are no abnormally close 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*- and *n*-glide planes present in the centrosymmetric space group *C*2/*c*. The molecular geometry and atomic labelling scheme is depicted in Fig. 1, while a stereoscopic view of the molecule is provided by Fig. 2. Interatomic distances and angles, along with their esd's, are collected in Tables 3 and 4, respectively.

The molecule possesses a tetrahedral $W_2Ir_2$ core in which the homonuclear distances are W(1)–W(2) 2.995(1) Å and Ir(1)–Ir(2) 2.653(1) Å. The four heteronuclear distances are, in decreasing order, Ir(1)–W(1) 2.825(1), Ir(1)–W(2) 2.802(1), Ir(2)–W(2) 2.784(1) and Ir(2)–W(1) 2.781(1) Å; aver. (Ir–W) 2.798 Å. These bond lengths are similar to those found in the parent compound, $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ [2], viz., W–W 2.991(1), Ir–Ir 2.722(1) and Ir–W 2.796(1)–2.863(1) Å (aver. 2.835 Å).

The cluster as a whole is associated with the expected 60 outer valence electrons (i.e., two $d^6$ $W^0$ atoms, two $d^9$ $Ir^0$ atoms, two electrons from each of seven carbonyl ligands, five electrons from each of the two $\eta^5$-cyclopentadienyl systems, two electrons from the $\mu$-$CHCO_2Et$ ligand and four electrons from the $\mu_3$-$CHCO_2Et$ ligand). Nevertheless, the distribution of electrons is not uniform. Each iridium atom is linked to two terminal carbonyl ligands, but Ir(2) is bonded (through C(5))

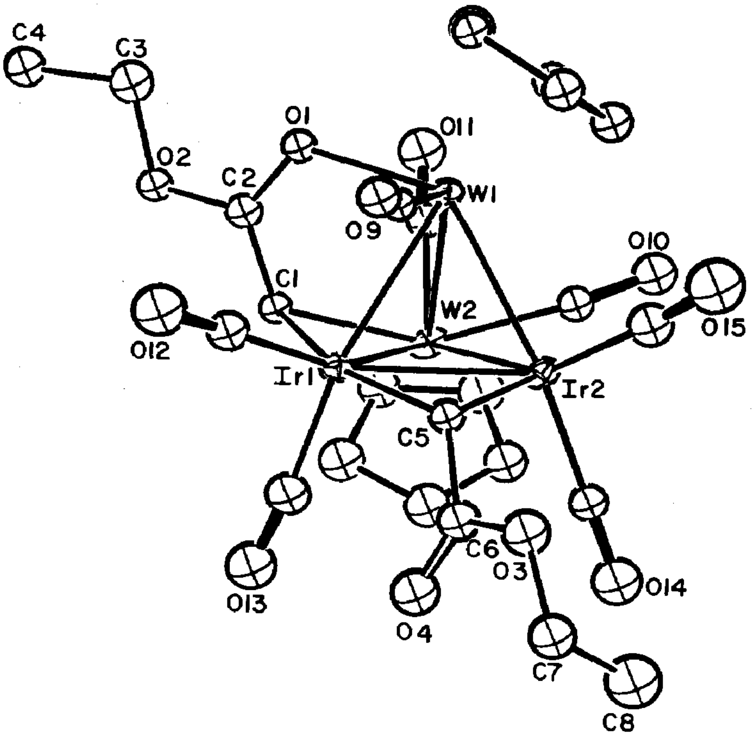

Fig. 1. Labelling of atoms in the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ molecule (ORTEP2 diagram; 30% probability ellipsoids). Note that "semi-bridging" M···CO interactions have not been drawn in (see text). Note that Ir(2)...C(10) is 2.307(16) Å.

to only one $CHCO_2Et$ ligand whereas Ir(1) is bonded to both $CHCO_2Et$ ligands (though C(1) and C(5)). Each tungsten atom is attached to an $\eta^5$-cyclopentadienyl ligand. W(1) is linked to a single carbonyl ligand and to the $\mu_3$-$CHCO_2Et$ ligand though O(1) of the ester group. In contrast to this, W(2) is associated with two carbonyl ligands and is linked (though C(1)) to the same $\mu_3$-$CHCO_2Et$ ligand.

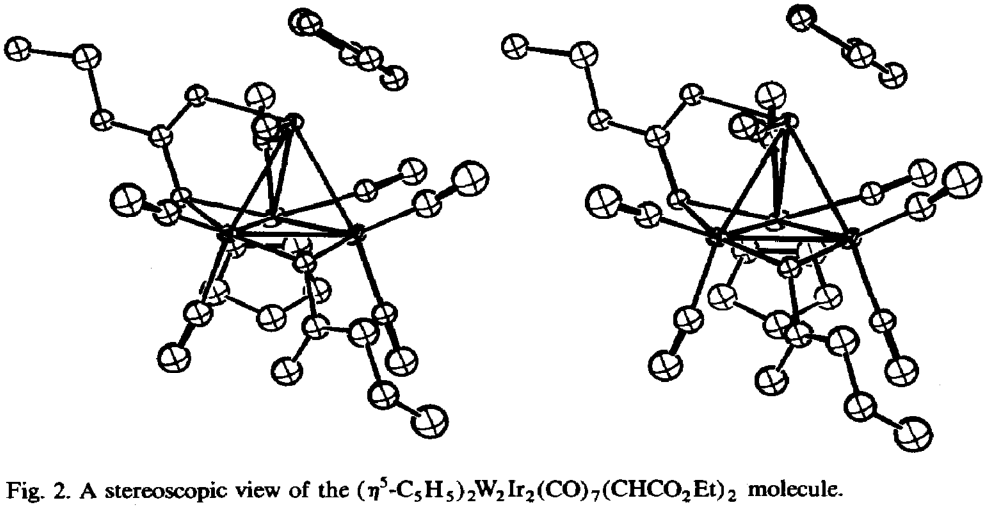

Fig. 2. A stereoscopic view of the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ molecule.

Table 3

Interatomic distances (Å) and esd's for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| *(A) Metal – metal distances* | | | |
| W(1)–W(2) | 2.995(1) | Ir(1)–Ir(2) | 2.653(1) |
| W(1)–Ir(1) | 2.825(1) | W(2)–Ir(1) | 2.802(1) |
| W(1)–Ir(2) | 2.781(1) | W(2)–Ir(2) | 2.784(1) |
| *(B) Metal – $CHCO_2Et$ distances* | | | |
| Ir(1)–C(1) | 2.144(15) | Ir(1)–C(5) | 2.113(15) |
| W(2)–C(1) | 2.193(14) | Ir(2)–C(5) | 2.110(5) |
| W(1)–O(1) | 2.154(10) | | |
| *(C) Distances within the $CHCO_2Et$ ligands* | | | |
| C(1)–C(2) | 1.427(22) | C(5)–C(6) | 1.449(23) |
| C(2)–O(1) | 1.264(18) | C(6)–O(4) | 1.239(21) |
| C(2)–O(2) | 1.336(19) | C(6)–O(3) | 1.338(21) |
| O(2)–C(3) | 1.454(22) | O(3)–C(7) | 1.452(22) |
| C(3)–C(4) | 1.484(25) | C(7)–C(8) | 1.393(30) |
| *(D) M – CO and C – O distances* | | | |
| W(1)–C(9) | 1.940(15) | C(9)–O(9) | 1.164(19) |
| W(2)–C(10) | 2.055(16) | C(10)–O(10) | 1.200(20) |
| W(2)–C(11) | 1.918(17) | C(11)–O(11) | 1.186(22) |
| Ir(1)–C(12) | 1.862(17) | C(12)–O(12) | 1.184(23) |
| Ir(1)–C(13) | 1.889(19) | C(13)–O(13) | 1.165(23) |
| Ir(2)–C(14) | 1.897(17) | C(14)–O(14) | 1.168(23) |
| Ir(2)–C(15) | 1.832(19) | C(15)–O(15) | 1.153(25) |
| *(E) Possible semibridging M... CO distances < 3Å* | | | |
| Ir(2)...C(10) | 2.307(16) | W(1)...C(11) | 2.934(18) |
| Ir(1)...C(9) | 2.757(14) | W(1)...C(10) | 2.945(16) |
| *(F) W – ($\eta^5$-$C_5H_5$) distances* | | | |
| W(1)–Cp(1) | 2.369(17) | W(2)–Cp(6) | 2.390(21) |
| W(1)–Cp(2) | 2.334(17) | W(2)–Cp(7) | 2.394(21) |
| W(1)–Cp(3) | 2.278(17) | W(2)–Cp(8) | 2.300(19) |
| W(1)–Cp(4) | 2.284(16) | W(2)–Cp(9) | 2.331(22) |
| W(1)–Cp(5) | 2.345(19) | W(2)–Cp(10) | 2.328(20) |
| W(1)–Cp [a] | 1.984 | W(2)–Cp [a] | 2.021 |
| *(G) C – C distances within the cyclopentadienyl ligands* | | | |
| Cp(1)–Cp(2) | 1.437(25) | Cp(6)–Cp(7) | 1.450(29) |
| Cp(2)–Cp(3) | 1.427(25) | Cp(7)–Cp(8) | 1.328(27) |
| Cp(3)–Cp(4) | 1.451(23) | Cp(8)–Cp(9) | 1.419(30) |
| Cp(4)–Cp(5) | 1.400(25) | Cp(9)–Cp(10) | 1.398(28) |
| Cp(5)–Cp(1) | 1.379(25) | Cp(10)–Cp(6) | 1.452(28) |
| average | 1.419 ± 0.029 | Average | 1.409 ± 0.051 |

[a] Cp is the centroid of the appropriate $\eta^5$-$C_5H_5$ ligand.

Formal electron counting shows that Ir(1) and W(1) are each associated with 18 outer-valence electrons, W(2) with 19 and Ir(2) with 17.

The formally electron-rich nature of W(2) and electron-poor nature of Ir(2) are balanced by electron donation through a "semi-bridging" interaction [16] of the carbonyl group C(10)–O(10) with Ir(2). Thus, the W(2)–C(10) bond of 2.055(16) Å

Table 4

Selected interatomic angles (deg) and esd's for $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| *(A) Intermetallic angles* | | | |
| W(1)–W(2)–Ir(1) | 58.22(2) | W(1)–Ir(1)–Ir(2) | 60.92(2) |
| W(1)–W(2)–Ir(2) | 57.39(2) | W(2)–Ir(1)–Ir(2) | 61.31(2) |
| Ir(1)–W(2)–Ir(2) | 56.71(2) | W(1)–Ir(1)–W(2) | 64.32(2) |
| W(2)–W(1)–Ir(1) | 57.46(2) | W(1)–Ir(2)–Ir(1) | 62.61(2) |
| W(2)–W(1)–Ir(2) | 57.49(2) | W(2)–Ir(2)–Ir(1) | 61.98(2) |
| Ir(1)–W(1)–Ir(2) | 56.48(2) | W(1)–Ir(2)–W(2) | 65.12(2) |
| *(B) C–M–M and M–C–M angles involving the $CHCO_2Et$ ligands* | | | |
| C(1)–Ir(1)–Ir(2) | 109.75(39) | C(5)–Ir(1)–Ir(2) | 51.03(40) |
| C(1)–Ir(1)–W(1) | 75.71(39) | C(5)–Ir(1)–W(1) | 90.47(40) |
| C(1)–Ir(1)–W(2) | 50.52(39) | C(5)–Ir(1)–W(2) | 111.36(40) |
| C(1)–W(2)–Ir(1) | 49.01(38) | C(5)–Ir(2)–Ir(1) | 51.14(40) |
| C(1)–W(2)–W(1) | 71.40(38) | C(5)–Ir(2)–W(1) | 91.76(40) |
| C(1)–W(2)–Ir(2) | 103.84(38) | C(5)–Ir(2)–W(2) | 112.2(40) |
| Ir(1)–C(1)–W(2) | 80.47(50) | Ir(1)–C(5)–Ir(2) | 77.83(50) |
| *(C) Angles within the $CHCO_2Et$ ligands* | | | |
| C(1)–C(2)–O(1) | 123.1(14) | C(5)–C(6)–O(4) | 125.9(16) |
| C(1)–C(2)–O(2) | 119.3(14) | C(5)–C(6)–O(3) | 112.2(14) |
| O(1)–C(2)–O(2) | 117.5(14) | O(4)–C(6)–O(3) | 121.9(16) |
| C(2)–O(2)–C(3) | 118.1(12) | C(6)–O(3)–C(7) | 120.3(14) |
| O(2)–C(3)–C(4) | 110.7(14) | O(3)–C(7)–C(8) | 112.2(16) |
| C(2)–O(1)–W(1) | 116.6(10) | | |
| *(D) Metal–carbon–oxygen angles* | | | |
| W(1)–C(9)–O(9) | 168.6(13) | Ir(1)–C(12)–O(12) | 176.9(15) |
| W(2)–C(10)–O(1) | 153.1(13) | Ir(1)–C(13)–O(13) | 172.7(16) |
| W(2)–C(11)–O(11) | 171.9(15) | Ir(2)–C(14)–O(14) | 179.3(15) |
| | | Ir(2)–C(15)–O(15) | 174.1(18) |
| Ir(1) ··· C(9)–O(9) | 119.8(11) | Ir(2) ··· C(10)–O(10) | 127.5(12) |
| W(1) ··· C(11)–O(11) | 115.2(12) | W(1) ··· C(10)–O(10) | 121.9(12) |
| *(E) Angles within the cyclopentadienyl ligands* | | | |
| Cp(5)–Cp(1)–Cp(2) | 108.9(15) | Cp(10)–Cp(6)–Cp(7) | 106.7(17) |
| Cp(1)–Cp(2)–Cp(3) | 106.1(15) | Cp(6)–Cp(7)–Cp(8) | 106.1(18) |
| Cp(2)–Cp(3)–Cp(4) | 108.4(15) | Cp(7)–Cp(8)–Cp(9) | 113.9(18) |
| Cp(3)–Cp(4)–Cp(5) | 106.1(14) | Cp(8)–Cp(9)–Cp(10) | 105.2(18) |
| Cp(4)–Cp(5)–Cp(1) | 110.6(16) | Cp(9)–Cp(10)–Cp(6) | 108.1(18) |

is longer than the other W–CO bonds (cf. W(1)–C(9) 1.940(15) Å and W(2)–C(11) 1.918(17) Å; average 1.929 ± 0.016 Å), and is accompanied by the "semi-bridging" interaction Ir(2) ··· C(10) 2.307(16) Å, with angle W(2)–C(10)–O(10) 153.1(13)° and angle Ir(2) ··· C(10)–O(10) 127.5(12)°. The "$\alpha$-value" for this interaction defined [17] as $(d_2 - d_1)/d_1$ (where $d_1$ is the shorter M–CO distance and $d_2$ is the longer M–CO distance) is 0.12; this is at the "strong interaction" end of the range ($\alpha = 0.1$–$0.6$) that Curtis et al. [16] define as the semi-bridging regime. It should be emphasized that the heteronuclear nature of the semi-bridged W(2)–Ir(2) linkage, coupled with internally calculated atomic radii of $r$(W) 1.498 Å (from W(1)–W(2) 2.995(1) Å) and $r$(Ir) 1.327 Å (from Ir(1)–Ir(2) 2.653(1) Å), lead to a "partially-corrected $\alpha$-value" of 0.21, which we believe to be a more realistic value. Here we define the "partially-corrected $\alpha$-value" as $[(d_1 - r(M_1)) - (d_2 - r(M_2))]/d_1$. We see no unique way of correcting the denominator ($d_1$) for differences in radii between $M_1$ and $M_2$. Clearly, however, the interaction is of a "semi-bridging" rather than simple "$\mu_2$-bridging" nature.

The remaining W–C–O systems show substantial deviations from linearity and some possible very weak interactions with other metal atoms. These are of far less importance than the W(2)–C(10) · · · Ir(2) interaction and could simply result from the crowding of ligands on the coordination surface of the $W_2Ir_2$ cluster. In decreasing order of importance there are as follows:

(i) angle W(1)–C(9)–O(9) 168.6(13)°, with W(1)–C(9) 1.940(15) Å and Ir(1) · · · C(9) 2.757(14)Å, yielding $\alpha = 0.42$ and $\alpha$(partially corrected) = 0.51 for the W(1)–C(9) · · · Ir(1) interaction;

(ii) angle W(2)–C(11)–O(11) 171.9(15)°, with W(2)–C(11) 1.918(17) Å and W(1) · · · C(11) 2.934(18)° with $\alpha = 0.53$ for the W(2)–C(11) · · · W(1) interaction;

(iii) a second weak interaction of W(2)–C(10)–O(10) with another metal atom; thus W(1) · · · C(10) 2.945(16) Å as compared to W(2)–C(10) 2.055 (16) Å, providing $\alpha = 0.43$ for the W(2)–C(10) · · · W(1) interaction.

In contrast to the above, the Ir–C–O systems are close to linear (172.7(16)–179.3(15)°) and Ir-CO distances are internally consistent (1.832(15)–1.897(17) Å, average 1.870 ± 0.029 Å).

The most interesting feature of the structure is the presence of two bridging $CHCO_2Et$ ligands which are linked by two different modes to the tetrahedral $W_2Ir_2$ cluster. The $CHCO_2Et$ ligand with C(5) as its $\alpha$-carbon atom bridges the Ir(1)–Ir(2) linkage symmetrically, with Ir(1)–C(5) 2.113(15) Å and Ir(2)–C(5) 2.110(15) Å (average 2.112 ± 0.002 Å); the angle Ir(1)–C(5)–Ir(2) is 77.83(50)°. Other dimensions in this ligand are normal, with C(5)–C(6) 1.449(23) Å, C(6)–O(3) 1.338(21) Å and C(6)=O(4) 1.239(21) Å.

The second $CHCO_2Et$ ligand, with C(1) as its $\alpha$-carbon atom, caps the cluster face Ir(1)–W(1)–W(2) in a $\mu_3$-$\eta^2$ mode. Thus, C(1) bridges the Ir(1)–W(2) linkage with Ir(1)–C(1) 2.144(15) Å, W(2)–C(1) 2.193(14) Å and angle Ir(1)–C(1)–W(2) 80.47(50)°. In addition, O(1), the ketonic oxygen atom of the ester group, provides a $\sigma$-donor linkage to W(1), with W(1)–O(1) 2.154(10) Å. Other dimensions in this ligand include C(1)–C(2) 1.427(22) Å, C(2)–O(2) 1.336(19) Å and C(2)=O(1) 1.264(18) Å. The increase in C(2)=O(1) relative to C(6)=O(4) is in the expected direction but is not statistically significant beyond the 1.3$\sigma$ level.

The parent molecule $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ [2] is known to have a crowded coordination surface and it is probably impossible to replace two carbonyl groups by $\mu$-$CHCO_2Et$ ligands to form $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_8(\mu\text{-}CHCO_2Et)_2$ because of the greater cone angle of $\mu$-$CHCO_2Et$ versus CO. The observed product $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(\mu\text{-}CHCO_2Et)(\mu_3\text{-}\eta^2\text{-}C,C,O\text{-}CHCO_2Et)$, in which three carbonyl groups are replaced by two $CHCO_2Et$ groups, is presumably the lowest energy sterically attainable structure with the minimum number of carbonyls removed.

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

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