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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2Et)_2$, A TETRAHEDRAL HETEROMETAL CLUSTER WITH TWO DIFFERENT ENVIRONMENTS FOR ETHYLCARBOXYLATOCARBENE LIGANDS

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Summary

The tetrahedral heteronuclear cluster complex $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ reacts with N_2CHCO_2R (R = Et, Me) at room temperature to form the dicarbene species $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_7(CHCO_2R)_2$. An X-ray diffraction study (R = Et) shows an intact tetrahedral metal framework with two distinct sites for the $CHCO_2Et$ ligands. The first uses its carbon atom to bridge the Ir—Ir bond; the second uses its carbon atom to bridge an Ir—W bond and, additionally, forms a donor bond from a carbonyl oxygen atom to the second tungsten atom.

We have reported previously the syntheses [1] and structures of $CpWIr_3(CO)_{11}$ [2] ($Cp = \eta^5\text{-}C_5H_5$) and $Cp_2W_2Ir_2(CO)_{10}$ [3] along with their utility as precursors to alumina-supported bimetallic particles [1]. In order to determine how these supported particles might interact with organic substrates on a molecular level, we have begun to investigate their reactivity in solution. We have shown previously [4] that $Cp_2W_2Ir_2(CO)_{10}$ reacts with disubstituted acetylenes (C_2R_2) by two independent pathways; cleavage of a W—W bond to form the "butterfly" cluster $Cp_2W_2Ir_2(CO)_8(C_2R_2)$ and cleavage of a W—Ir bond to form the reorganized alkylidynedimetallaallyl species $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CR)(\mu_3\text{-}\eta^3\text{-}C_3R_3)$. We now report on the reaction of $Cp_2W_2Ir_2(CO)_{10}$ with alkyl diazocarboxylates.

Treatment of $Cp_2W_2Ir_2(CO)_{10}$ (~20 mg in ~20 ml CH_2Cl_2) with excess

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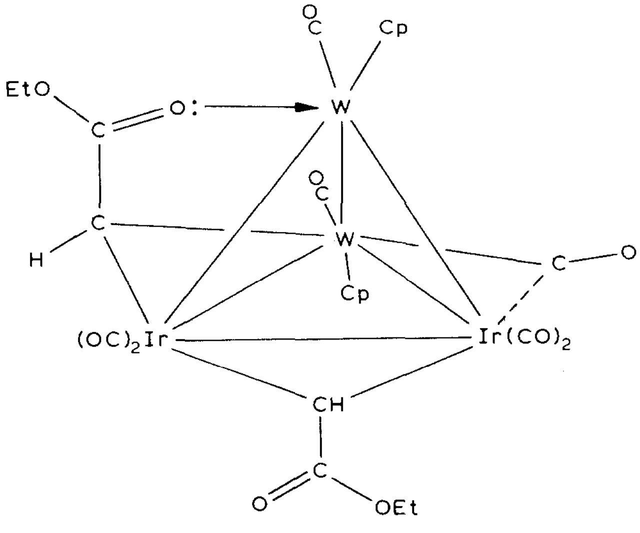
N_2CHCO_2Et (~9 μl) at room temperature yielded, after stirring for 1 h and TLC deep purple $Cp_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ (46%)*. The complex $Cp_2W_2Ir_2(CO)_7(CHCO_2Me)_2$ ** was similarly formed (50% yield) from N_2CHCO_2Me. We have completed a single-crystal X-ray diffraction study on $Cp_2W_2Ir_2(CO)_7(CHCO_2Et)_2$ and show it to possess two very different $CHCO_2Et$ ligands.

Crystal data: $C_{25}H_{22}O_{11}W_2Ir_2$, $M = 1250.6$, monoclinic, space group $C2/c$, a 34.0974(52), b 8.7057(12), c 19.8106(31) Å, β 111.053(12)°, U 5488.1(15) $Å^3$, D_c 3.30 g cm^{-3}, $Z = 8$, μ(Mo-K_α) 191.6 cm^{-1}. Diffraction data (Mo-K_α radiation) were collected with a Syntex $P2_1$ four-circle diffractometer [5]. All non-hydrogen atoms were accurately located; hydrogen atoms were included in calculated positions [6]. Convergence was reached with R 4.7% for all 3621 data (2θ 4.5—45.0°) against 181 variables (NO/NV 20.0/1) and R 3.9% for those 3216 data with $|F_o| > 3\sigma(|F_o|)$. The resulting structure is illustrated in Fig. 1 and may be formally represented by I. The W_2Ir_2 core retains its tetrahedral geometry, with metal—metal distances (in Å) being as follows: W(1)—W(2) = 2.995(1), W(1)—Ir(1) 2.825(1), W(1)—Ir(2) 2.781(1), W(2)—Ir(1) 2.802(1), W(2)—Ir(2) 2.784(1) and Ir(1)—Ir(2) 2.653(1). Each iridium atom is linked to two terminal carbonyl ligands (Ir—CO 1.832(19)—1.897(17) Å).



(I)

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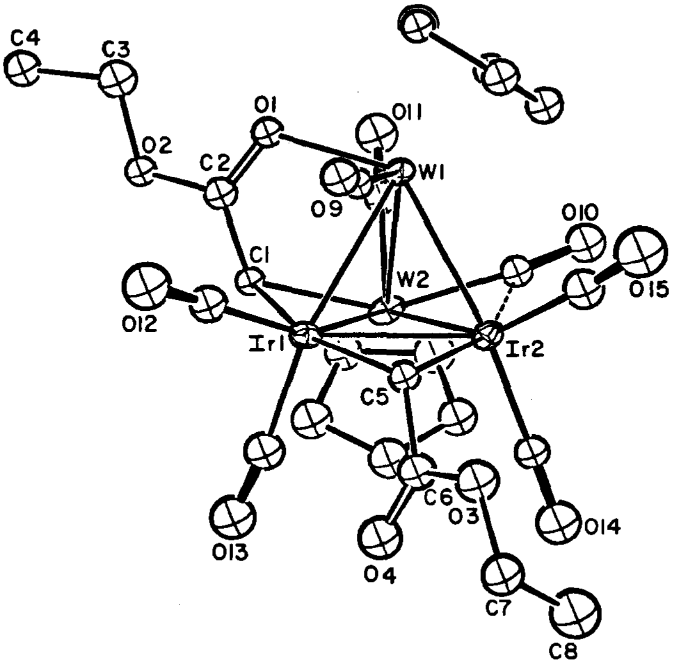
*[$Cp_2W_2Ir_2(CO)_7(CHCO_2Et)_2$]: ^1H NMR ($CDCl_3$): δ 11.08 (1H, s, CH), 6.68 (1H, s, CH), 5.64 (5H, s, Cp), 4.94 (5H, s, Cp), 4.14 (2H, q, J 7 Hz, CH_2), 3.96 (2H, q, J 7 Hz, CH_2), 1.29 (3H, t, CH_3), 1.21 (3H, t, CH_3) ppm; IR (C_6H_{12}, ν(CO): 2051(s), 2018(vs), 2006(s,sh), 1976(m), 1887(m), 1854(m), 1788(m), 1702(w) cm^{-1}; MS (FAB) m/z 1250 (M^+), 1250 — 28x, x = 1—5; Anal. Found: C, 24.07; H, 1.90. $C_{25}H_{22}O_{11}W_2Ir_2$ calcd.: C, 24.01; H, 1.77%.

**[$Cp_2W_2Ir_2(CO)_7(CHCO_2Me)_2$]: ^1H NMR ($CDCl_3$): δ 11.05 (1H, s, CH), 6.67 (1H, s, CH), 5.65 (5H, s, Cp), 4.95 (5H, s, Cp), 3.72 (3H, s, CH_3), 3.58 (3H, s, CH_3) ppm; ^{13}C NMR (CD_2Cl_2, 20° C): δ 240.2 (J(WC) 176 Hz), 230.1 (J(WC) 164 Hz), 219.8 (J(WC) 98 Hz), 189.8, 182.5, 178.7, 173.5 ppm; IR (C_6H_{12}, ν(CO)): 2051(s), 2018(vs), 2006(s,sh), 1976(m), 1889(m), 1857(m), 1791(m); 1702(w) cm^{-1}; MS (FAB), m/z 1222 (M^+), 1222 — 28x, x = 1—6; Anal. Found: C, 22.87; H, 1.50. $C_{23}H_{18}O_{11}W_2Ir_2$ calcd.: C, 22.60; H, 1.48%.



Each tungsten atom is linked to a Cp ligand and to one terminal carbonyl (W—CO 1.918(17)–1.940(15) Å); atom W(2) is additionally linked to a second carbonyl ligand which is involved in a "semi-bridging" linkage to Ir(2) (W(2)—C(10) 2.055(16) Å, Ir(2)···C(10) 2.307(16) Å, angle W(2)—C(10)—O(10) 153.1(13)°, Ir(2)···C(10)—O(10) 127.5(12)°).

One $CHCO_2Et$ ligand is in a typical bridging position across the short homonuclear Ir(1)—Ir(2) bond, with Ir(1)—C(5) 2.113(15) Å and Ir(2)—C(5) 2.110(15) Å. The second $CHCO_2Et$ ligand bridges the heteronuclear Ir(1)—W(2) linkage, with Ir(1)—C(1) 2.144(15) Å and W(2)—C(1) 2.193(14) Å; in addition the carbonyl function of the ester is involved in a donor bond to W(1) with O(1) → W(1) 2.154(10) Å. (The C(2)—O(1) distance of 1.264(18) Å is not significantly greater than the uncoordinated C(6)—O(4) bond length of 1.239(23) Å.)

The following chemical points should be noted: (1) $Cp_2W_2Ir_2(CO)_{10}$ shows remarkable reactivity for a saturated (60-electron) cluster, much more so than for the related homonuclear species $Ir_4(CO)_{12}$.

(2) In contrast to the reactions of $Cp_2W_2Ir_2(CO)_{10}$ with C_2R_2, substitution of $CHCO_2R$ for CO occurs with retention of the closed W_2Ir_2 frame.

(3) The locations of the $CHCO_2R$ units are across the stronger (shorter) metal—metal bonds: Ir—Ir and Ir—W. In contrast to this, C_2R_2 leads to cleavage of the weak bonds: W—W (preferentially) and Ir—W.

(4) The large difference between ^1H NMR resonances of the *α-CH* protons is probably due to chelation causing a high field shift.

(5) W—(CO)···Ir bridging clearly leads to an upfield ^{13}C NMR shift as revealed by diminishing $J(^{13}C—^{183}W)$.

(6) Despite having a semi-bridging carbonyl ligand, the compound is not fluxional below its decomposition temperature (85°C in toluene).
(7) The complex cannot be formed by interaction of $RCO_2CH{=}CHCO_2R$ with $Cp_2W_2Ir_2(CO)_{10}$ nor by direct hydrogenation of $Cp_2W_2Ir_2(CO)_8[C_2(CO_2Et)_2]$.

Additional tabular data on this structural study is available on request from M.R.C.

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