$[Ir_4(CO)_8\{(MeCO_2)_2C_2\}_4]$: a Rectangular Cluster

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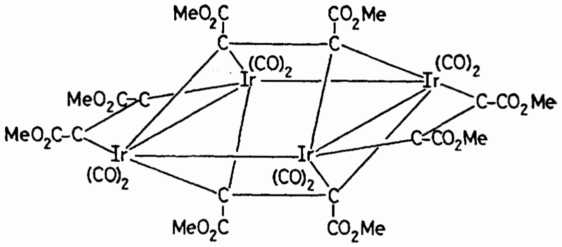
Summary $[Ir_4(CO)_8\{(MeCO_2)_2C_2\}_4]$ has been prepared from the reaction of $[Ir_4(CO)_{12}]$ and $(MeCO_2)_2C_2$; the molecular structure has been established by *X*-ray analysis.

TRANSITION metal clusters exist in a wide range of geometrical forms. In this communication we report an Ir_4 cluster which possesses an unusual rectangular geometry. The complex also contains four acetylene ligands: two functioning as four-electron donors and two as two-electron donors.

Irradiation of finely divided $[Ir_4(CO)_{12}]$, in benzene, in the presence of an excess of $(MeCO_2)_2C_2$ at *ca.* 25 °C for 24 h gives a dark red-brown solution from which purple crystals of $[Ir_4(CO)_8\{(MeCO_2)_2C_2\}_4]$ (I) may be separated in *ca.* 35% yield. The i.r. spectrum of this complex in $CHCl_3$ is simple, exhibiting two strong bands at 2096 and 2068 (ν_{CO}) cm^{-1}. In the mass spectrometer only ions corresponding to an Ir_3 species were observed and, in view of the *X*-ray analysis, we believe that decomposition occurs. The molecular structure of the complex has been determined by single crystal *X*-ray analysis.



(I)

Crystal data: $C_{32}H_{24}Ir_4O_{24}$, $M = 1561{\cdot}3$, monoclinic, $a = 20{\cdot}663(15)$, $b = 9{\cdot}133(20)$, $c = 21{\cdot}701(16)$ Å, $\beta = 105{\cdot}44(10)°$, $U = 3947{\cdot}5$ Å^3; $D_c = 2{\cdot}63$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 134{\cdot}5$ cm^{-1}, space group $C2/c$. 3613 intensities (layers 0–*h*,13,*l*) were recorded on a Stoe STADI-2 two-circle diffractometer using graphite-monochromated Mo-K_α radiation. An empirical absorption correction was applied, and the 2655 unique observed intensities $[I > 1{\cdot}5\sigma(I)]$ were used in structure solution. The fractional atomic co-ordinates of the two unique iridium atoms were located by multisolution Σ_2 sign expansion, and those of the light atoms from subsequent Fourier difference maps. The methyl hydrogen atoms were constrained to lie 1·08 Å from the carbon atoms, defining three vertices of a tetrahedron. Full-matrix least-squares refinement (with Ir anisotropic, C and O individual isotropic, H common isotropic temperature factor) yielded a converged R of 0·025, and a corresponding $R_w\ [=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0{\cdot}023$.

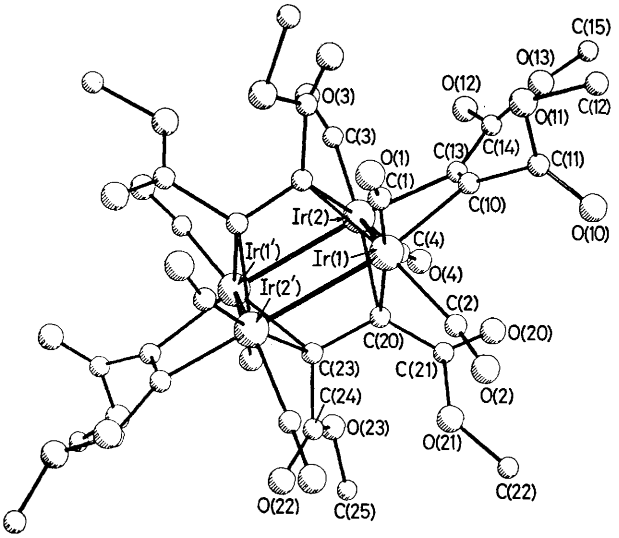


FIGURE. The molecular structure of $[Ir_4(CO)_8\{(MeCO_2)_2C_2\}_4]$, hydrogen atoms have been omitted for clarity. Bond lengths: Ir(1)–Ir(2), 2·715(1); Ir(1)–Ir(2'), 2·810(1); Ir(2)–Ir(1'), 2·810(1); Ir(1)–C(10), 2·127(9); Ir(2)–C(13), 2·095(7); Ir(1)–C(20), 2·136(7); Ir(2)–C(20), 2·117(8); Ir(1')–C(23), 2·161(7); Ir(2')–C(23), 2·120(7), C(10)–C(13), 1·278(11); and C(20)–C(23), 1·446(9) Å; bond angles: Ir(2)–Ir(1)–Ir(2'), 89·2(1) and Ir(1)–Ir(2)–Ir(1'), 90·8(1)°.

The molecular geometry of $[Ir_4(CO)_8\{(MeCO_2)_2C_2\}_4]$ is shown in the Figure, which includes some of the important bond lengths and angles. The complex is centrosymmetric, and the four iridium atoms define a rectangle. The two short Ir–Ir edges are bridged by two of the substituted acetylene ligands. The other two acetylenic ligands lie 1·50 Å above and below the metal plane, capping the rectangular faces, with the acetylenic C–C bonds approximately parallel with the longer Ir–Ir edges. Each iridium is also bonded to two terminal carbonyl ligands, giving a metal co-ordination number of eight.†

This structure appears to be the first crystallographic evidence for a cluster containing a rectangular planar arrangement of iridium atoms. Square-planar, doubly face-capped complexes are rare, but in $[Fe_4(CO)_{11}(NEt)(ONEt)]$,[1] the Fe_4 configuration is similar to that in the present work. The shorter of the two unique Ir–Ir bonds is longer than the values found in $[Ir_4(CO)_{12}]$[2] (two unique distances, 2·679 and 2·692 Å), but is in good agreement with the value of 2·717(3) Å in $[Ir_2(NO)_4(PPh_3)_2]$;[3] the longer bond is one of the longest reported where there is direct interaction between the metals.

The acetylenic C–C distances in the edge-bridging ligands show that the bonds have retained at least olefinic character. The bond lengths are similar to the values of 1·230(6) and 1·26(5) Å found in the diphenylacetylene ligands in $[Pt(C_2Ph_2)_2]$ and $[Pt_2(PMe_3)_2(C_2Ph_2)_2]$,[4] where the acetylene is bonded to one metal only. The face-capping acetylenic C – C distances indicate that the bonds have been reduced beyond olefinic character, and agree well with the C – C distance of 1·439(10) Å in $[Os_3(CO)_{10}(C_2Ph_2)]$,[5] where the ligand bridges two metal atoms. Thus the edge-bridging acetylenes donate two electrons each to the complex, and the face-capping ligands four. This results in a 64-electron system.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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