# Preparation, Identification, and Crystal Structure of a Novel Hexanuclear Iridium–Copper Cluster Complex

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*Summary* $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ has been synthesized from $IrCl(CO)(PPh_3)_2$ and $[Cu(C{\equiv}CPh)]_n$ and its molecular structure determined *via* *X*-ray diffraction; the six metal atoms define an octahedron in which two $PPh_3Ir$ moieties are mutually *trans*, four $(C{\equiv}CPh)$ units are $\sigma$-bonded to each Ir atom, and two $(C{\equiv}CPh)$ units (one from each Ir) form $\pi$-linkages to each of the four equatorial copper atoms.

THE formation of homo-atomic polynuclear clusters by the Group IB elements in their low-valent complexes is well-documented, examples being $[CuI(AsMe_3)]_4$,[1] $[HCu(PPh_3)]_6$,[2] $[Cu(m\text{-}CF_3C_6H_4)]_8$,[3] and $[Au_{11}(SCN)_3(PPh_3)_7]$.[4] We have now found that reactions between Group IB acetylides and co-ordinatively-unsaturated transition metal complexes are a fruitful source of hetero-atom clusters, and afford many different and novel types of complex.

The reaction between $IrCl(CO)(PPh_3)_2$ and copper phenylacetylide, carried out in refluxing benzene for 36 h, gives a dark coloured solution. From this may be obtained, after chromatography and crystallization, a 60% yield of beautiful purple crystals, which have a greenish yellow iridescence. This complex (I), is accompanied by smaller amounts of $Cu_2Cl_2(PPh_3)_3$ and $Ph_3PO$. From some experiments, small quantities of other heteronuclear cluster complexes, as yet not fully characterized, were also obtained.

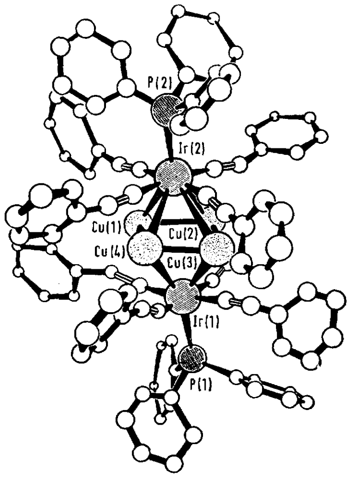

FIGURE 1. *The molecular stereochemistry of* $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$. *The phenyl group of the phenyl acetylide ligand* $\sigma$*-bonded to* Ir(1) *and* $\pi$*-bonded to* Cu(2) *has been omitted for the sake of clarity.*

Complex (I), m.p. 235°, was shown to have the formula $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$ by a full analysis and osmometric molecular weight determination. The complex is air-stable, and is soluble in benzene, dichloromethane, and acetone. The i.r. spectrum shows no ν(CO) bands; broad absorptions at 2017w, 2001w, and 1975w $cm^{-1}$ are assigned to complexed carbon–carbon triple bond stretching modes. The $^1H$ n.m.r. spectrum of complex (I) is not very informative, but that of the analogous complex containing diphenylmethylphosphine shows an apparent triplet at $\tau$ 6·98 for the methyl resonance. This feature suggests that the two phosphine ligands are *trans*, and could arise if the two iridium atoms are at the apices of a $Cu_4Ir_2$ octahedron.

The detailed molecular geometry of this complex has now been elucidated *via* a single-crystal *X*-ray diffraction study. *Crystal data:* $C_{100}H_{70}Cu_4Ir_2P_2$, $M$ = 1972·2, monoclinic, $a$ = 14·86(2), $b$ = 22·04(4), $c$ = 13·62(2) Å, $\beta$ = 105·04(10)° $U$ = 4308 Å$^3$, $D_m$ = 1·59(3), $D_c$ = 1·52 g $cm^{-3}$, $Z$ = 2, space-group $P2_1$ ($C_2^2$; No. 4).

Diffraction data complete to sin $\theta$ = 0·80 (Cu-$K_\alpha$ radiation) were collected on a diffractometer and were corrected for Lorentz, polarization, and absorption ($\mu$ = 79·01 $cm^{-1}$) effects. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All 108 non-hydrogen atoms have been accurately located, the present discrepancy index being $R$ = 8·5% for the 4584 independent non-zero reflections.

The molecule contains a slightly irregular octahedral cluster of metal atoms in which the two iridium atoms are in mutually *trans* positions [see Figure 1]. Iridium–copper distances range from 2·775(4) to 2·959(4), averaging 2·871 Å; copper–copper distances range from 2·663(6) to 2·829(6), averaging 2·740 Å. Each iridium atom is bonded apically to a triphenylphosphine ligand with Ir–P = 2·251(7) and 2·270(7) Å. In addition, four phenylacetylide ligands are $\sigma$-bonded to each iridium atom with Ir–C = 1·980(27)—2·110(22), mean 2·044 Å; each acetylenic fragment simultaneously participates in an asymmetric $\pi$-interaction with a copper atom on the octahedral meridian.† The acetylenic carbon atoms $\alpha$ to the iridium atoms are closer to their respective copper atoms than are the $\beta$ acetylenic carbons. Distances, in Å, are: Cu ··· C($\alpha$) = 1·882(27) —2·078(23) [mean 1·989], Cu ··· C($\beta$) = 2·139(27) —2·258(29) [mean 2·186], and C($\alpha$)–C($\beta$) = 1·180(40)—1·293(37) [mean 1·226].

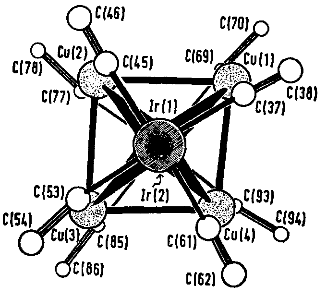

FIGURE 2. *The approximate* $D_4$ *symmetry of the* $Cu_4Ir_2P_2(C{\equiv}C)_8$ *'core' of the molecule.*

As shown in Figure 2, the $Cu_4Ir_2P_2(C{\equiv}C)_8$ core of the molecule has approximate $D_4$ symmetry. Finally we may note that the formal oxidation states of the metal atoms are $Cu^0$ and $Ir^{IV}$.

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† Simultaneous metal-acetylide $\sigma$-bonding and acetylide-metal $\pi$-bonding also occurs in such copper phenylacetylide complexes as $[Ph\text{-}C{\equiv}C\text{-}Cu]_n$ (ref. 5) and $[Ph\text{-}C{\equiv}C\text{-}CuPMe_3]_4$ (ref. 6).

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