H_5)Co($B_{10}C_2H_{12}$) referred to by Hawthorne and coworkers as "orange III" and "red-orange IV" (*cf.* ref 11). These two species produce crystals which are isomorphous since they each display apparent *mmm* (D_{2h}) Laue symmetry, identical systematic absences (*hkl* for $h + k = 2n + l$ and *h0l* for $l = 2n + 1$, consistent with the space group *Cmcm*, *Cmc*2$_1$, or *C*2*cm*), and very similar cell dimensions. For "orange III," $a = 7.259$ (3) Å, $b = 16.194$ (6) Å, $c = 11.052$ (2) Å, and $\rho_{\text{calcd}} = 1.371$ g cm^{-3} for $Z = 4$; for "red-orange IV," $a = 7.249$ (3) Å, $b = 16.258$ (7) Å, and $c = 11.199$ (5) Å, $\rho_{\text{obsd}} = 1.340$ (5) g cm^{-3}, and $\rho_{\text{calcd}} = 1.350$ g cm^{-3} for $Z = 4$. In addition, the species are almost certainly *isostructural* since careful study is required before intensity differences can be found between corresponding photographs.

Diffractometer data for each isomer were collected in a similar manner to that described in the Experimental Section. For each structure the following results were obtained. Routine structure-solving tactics led to marginally acceptable agreement ($R_F \approx 7\%$) only at the price of ridiculous anisotropic thermal parameters and fewer atoms than expected from the (well-established) empirical formulas. Ordinary Wilson-plot analyses of the *hk*0 and 0*kl* data gave scale factors essentially identical with those resulting from the remaining data, whereas at least one of these zones is expected to have twice the average intensity if the crystals are truly orthorhombic. We are led to believe that the crystals are not truly orthorhombic but are twinned monoclinic with β accidentally 90°. The most probable space group is *Cc* (since $Z = 4$ and the ^{11}B nmr spectra showed no molecular symmetry[11]). The hypothesized twinning relation has four equivalent descriptions: either a twofold rotation about, or a mirror perpendicular to, either of the monoclinic *a* or *c* axes. [This would superimpose the *hkl* and $hk\bar{l}$ reflections, while preserving the systematic absences for space group *Cc*.]

Our structure-solving efforts made prior to the discovery of twinning, coupled with later work with the 0*kl* and *hk*0 data (which should not be affected by the twinning), reveal (1) that the principal molecular axis lies nearly parallel to *b* and (2) that the cobalt atoms occupy pseudo special positions (at $y \approx 1/4$) such that they define a face-centered lattice and contribute only weakly to data with $h + l = 2n + 1$.

We have not continued with these studies, since it is most unlikely that even the most painstaking effort would enable us to achieve our principal goal, *i.e.*, that of distinguishing which of the cage positions was taken up by carbon and which by boron.

Registry No. (π-C_5H_5)Co(π-$B_{10}C_2H_{12}$), 37333-32-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1411.

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Crystal and Molecular Structure of $Cu_4Ir_2(PPh_3)_2(C\equiv CPh)_8$, a Novel Heteronuclear Octahedral Metal Cluster Complex

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The heteronuclear metal cluster complex bis(triphenylphosphine)octakis(phenylethynyl)tetracopperdiiridium(4*Cu-Cu*)-(8*Cu-Ir*), $Cu_4Ir_2(PPh_3)_2(C\equiv CPh)_8$, has previously been prepared *via* the reaction of IrCl(CO)$(PPh_3)_2$ with $[PhC\equiv CCu]_n$. The complex crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ (C_2^2; No. 4) with $a = 14.86$ (2) Å, $b = 22.04$ (4) Å, $c = 13.62$ (2) Å, and $\beta = 105.04$ (10)°. The observed density (1.59 (3) g cm^{-3}) may be compared to the value of 1.52 g cm^{-3} calculated for mol wt 1972 and $Z = 2$. X-Ray diffraction data to $\sin\theta = 0.80$ (Cu Kα radiation) were collected with a Supper-Pace diffractometer, using the ω-scan technique. The structure was solved by means of a combination of Patterson, Fourier, and least-squares refinement techniques. All 108 independent nonhydrogen atoms have been accurately located, the final discrepancy index being $R_F = 8.2\%$ for the 4584 independent nonzero (*i.e.*, $I > 3\sigma(I)$) reflections. The six metal atoms define a slightly irregular octahedron in which the two iridium atoms are in mutually trans positions. Interatomic distances are Ir–Cu = 2.776 (4)–2.959 (4) Å [average 2.870 Å] and Cu–Cu = 2.665 (6)–2.823 (5) Å [average 2.739 Å]. Each iridium atom is bonded apically to a triphenylphosphine ligand, with Ir(1)–P(1) = 2.248 (8) Å and Ir(2)–P(2) = 2.268 (7) Å. Four phenylethynyl [PhC≡C–] ligands are σ bonded to each iridium atom, with Ir–C(α) = 1.982 (26)–2.109 (21) Å [average 2.044 Å]. Each acetylenic fragment simultaneously participates in an asymmetric π interaction with a copper atom on the octahedral meridian, such that Cu· · ·C(α) = 1.871 (26)–2.076 (23) Å [average 1.986 Å] and Cu· · ·C(β) = 2.142 (26)–2.254 (28) Å [average 2.185 Å]. Each copper atom is thus bonded to two acetylenic moieties, one above and one below the equatorial plane; the central $Cu_4Ir_2P_2(C\equiv C)_8$ "core" of the molecule has approximate, but not exact, D_4 symmetry. The eight acetylenic bonds, C(α)–C(β), range from 1.181 (39) to 1.289 (35) Å, averaging 1.226 Å. The Ir–C(α)–C(β)–C(phenyl) dihedral angles range from 114.4 to 171.8°–*i.e.*, the Ir–C≡C–Ph systems adopt non-linear *transoid* configurations, in contrast to the *cis*-bent arrangement of R groups normally observed in species in which R–C≡C–R ligands are coordinated to one (or more) transition metal atom(s).

Introduction

Bruce and coworkers[1] have shown that the reaction of Vaska's compound, IrCl(CO)$(PPh_3)_2$, with copper phenylacetylide in benzene does not simply result in oxidative addition but, rather, yields the heteronuclear metal cluster complex $Cu_4Ir_2(PPh_3)_2(C\equiv CPh)_8$, along with other minor

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(1) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).

products. In view of our previous interest in octahedral metal cluster complexes[2-4] and the complicated stoichiometry of this new complex, we have subjected it to a three-dimensional single-crystal X-ray diffraction study. Our results are reported below.

Unit Cell and Space Group

The sample of $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ was supplied by Dr. M. I. Bruce of the University of Bristol (Bristol, England). After many unsuccessful attempts at recrystallization, a few crystals suitable for an X-ray diffraction study were obtained by the slow evaporation of a CH_2Cl_2–C_6H_{12} solution of the complex. The complex is air stable for indefinite periods and does not decompose upon exposure to X-rays.

Examination of the crystal habit and the observed reciprocal lattice symmetry (C_{2h}; $2/m$) indicated that the crystals belonged to the monoclinic system. A careful survey of $(0–1)kl$ and $h(0–1)l$ Weissenberg photographs and *a* and *b* axis oscillation photographs [all taken with Cu Kα radiation] along with $hk(0–1)$ and $(0–1)kl$ precession photographs and *a* and *c* "cone-axis" photographs [taken with Mo Kα radiation] revealed only the systematic absence $0k0$ for $k = 2n + 1$. This is compatible with the noncentrosymmetric space group $P2_1$ (C_2^2; No. 4)[5] or the centrosymmetric space group $P2_1/m$ (C_{2h}^2; No. 11).[6]

Unit cell dimensions, obtained from zero-level precession photographs taken at ambient temperatures (23 ± 2°) with Mo Kα radiation and calibrated with lead nitrate ($a_{23°} = 7.8566$ Å),[7] were $a = 14.86$ (2) Å, $b = 22.04$ (4) Å, $c = 13.62$ (2) Å, and $\beta = 105.04$ (10)°. The unit cell volume is 4308 Å^3. The observed density (1.59 ± 0.03 g cm^{-3}, by neutral buoyancy in aqueous ZnI_2 solution) is consistent with the value of 1.520 g cm^{-3} calculated for mol wt 1972 and $Z = 2$. The asymmetric unit is therefore either (i) one entire molecule, in space group $P2_1$, or (ii) one half-molecule, in space group $P2_1/m$. The successful elucidation of the crystal structure shows the former to be the case; thus, no crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

The complex crystallizes as large maroon parallelepipeds. All attempts to trim these crystals to dimensions more closely approaching optimum size (*i.e.*, thickness $< 2/\mu$) were thwarted by the extremely fragile texture of the crystals. Therefore two rather large crystals were used during the collection of intensity data; great care was taken to measure accurately the crystal dimensions for the purpose of making absorption corrections. Crystal A, mounted on its *a* axis, had dimensions 1.08 × 0.76 × 0.24 mm (relative to *a, b, c*, respectively), while the *b*-mounted crystal B had dimensions of 0.65 × 0.84 × 0.40 mm (along *a, b, c*, respectively).

For data collection, Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) was used (rather than the less absorbed Mo Kα radiation) in order to obtain more intensity. Data were collected on a Supper-Pace "Buerger Automated Diffractometer" using a stationary-background, ω-scan, stationary-background counting sequence and equiinclination Weissenberg geometry. The apparatus and *modus operandi* have been described at length elsewhere.[8] Details specific to the present analysis include the following: (1) generator conditions 49 kV/18 mA; (2) $d\omega/dt = 2°$ min^{-1}; (3) $\omega = [1.7 + (0.9/L)]°$ for crystal A and $[1.7 + (0.8/L)]°$ for crystal B; (4) check reflections collected after each batch of 40 reflections to monitor overall stability [no significant, *i.e.*, >2%, deviations were observed]; (5) initial and final backgrounds, B_1 and B_2 counts, each collected for one-fourth the time of the ω scan (C counts); (6) a large collimator (1.2-mm diameter) used at the X-ray source because of the unusually large crystal size.

The intensity, $I(hkl)$, of a reflection hkl was calculated by the expression $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$. Weights were assigned to the data according to the following scheme: $I(hkl) > I_{\min}$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $I(hkl) \leqslant I_{\min}$, $\sigma\{I(hkl)\} = 0.1[I_{\min}]^{1/2}\cdot[I(hkl)]^{1/2}$. Here $I_{\min}$ was chosen as 4900 counts. Data were subsequently rejected on two bases: (i) $I(hkl) \leqslant 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$, *i.e.*, reflection not more than 3σ above background; (ii) $B_1(hkl)/B_2(hkl)$ or $B_2(hkl)/B_1(hkl) > 3.0$—indicative of overlap of adjacent reflections or "streaking" from adjacent lower angle reflections.

Data for the quadrants hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ of levels $(0–6)kl$ were collected from crystal A, while data for the quadrants hkl and $\bar{h}kl$ of levels $h(0–21)l$ were collected from crystal B. Each level was complete to $\sin\theta = 0.80$ except for the few data in the sphere $0° \leqslant \theta \leqslant 4°$ which are inaccessible due to a Pb backstop behind the crystal. All data were corrected for Lorentz and polarization effects. Absorption corrections were applied;[9] with μ(Cu Kα) = 79.01 cm^{-1}, transmission factors ranged from 0.0489 to 0.2470 for data from crystal A (volume 0.0970 mm^3) and from 0.0605 to 0.1873 for data from crystal B (volume 0.0842 mm^3).

Data from the 29 Weissenberg levels were correctly merged to a common scale *via* a least-squares process which minimizes a set of residuals linear in the logarithms of the individual scale factors;[10] however, the quality of the data was only fair, since the most consistent fit for merging the two sets of data was 9.71% (based on F^2).[11a] The 5372 Laue-independent reflections from crystal *B* coupled with the 2851 appropriate Laue-independent reflections from crystal A gave rise to a total of 4584 independent nonzero[11b] reflections which were placed on an absolute scale by means of a Wilson plot (which also indicated an average overall thermal parameter of $\bar{B} = 2.52$ Å^2).

Solution and Refinement of the Structure

Unless stated otherwise, crystallographic calculations were performed with the CRYM system[12] on the Harvard University IBM 360/65 computer.

Scattering factors for neutral carbon and hydrogen were taken from ref 13. For phosphorus, copper, and iridium, the Hartree–Fock–Slater values of Hanson, *et al.*,[14] were used. The real and imaginary components of dispersion for P, Cu, and Ir were included in the calculations. [$\Delta f'$(Ir) = −5 to −6, $\Delta f''$(Ir) = +7 to +6; $\Delta f'$(Cu) = −2.1, $\Delta f''$(Cu) = +0.7; $\Delta f'$(P) = +0.2, $\Delta f''$(P) = +0.5 electron.][15,16]

The discrepancy index used below is defined as $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The residual minimized during the least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$.

A three-dimensional Patterson synthesis, which had been "sharpened" such that the average intensity was no longer θ dependent and from which the origin peak had been removed, revealed the approximate locations of all iridium and copper atoms and indicated that the true space group was $P2_1$. The origin of the unit cell was defined by assigning a value of 0 to the y coordinate of atom Ir(2).

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(2) $H_2Ru_6(CO)_{18}$: M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93, 5670 (1971); M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).

(3) $[Me_4N^+]_2[Fe_6(CO)_{16}C^{2-}]$: M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, 93, 3073 (1971).

(4) $H_6Cu_6(PPh_3)_6$: M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 11, 1818 (1972); S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *J. Amer. Chem. Soc.*, 93, 2063 (1971).

(5) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 79.

(6) Reference 5, p 93.

(7) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 122. This table gives $a_t = [7.8404 + 216 \times 10^{-6}(t - 21)]$ kX where t is in degrees centigrade and 1 kX = 1.00202 Å.

(8) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 1123 (1968).

(9) Using the FORTRAN IV program IMBIBE, by Dr. J. Wormald. This program is based on a gaussian quadrature numerical integration technique; see C. W. Burnham, *Amer. Mineral.*, 51, 159 (1966).

(10) A. D. Rae, *Acta Crystallogr.*, 19, 683 (1965).

(11) (a) With the noncentrosymmetric space group $P2_1$, anomalous dispersion causes a breakdown in the Friedel relationship such that $I(hkl) \neq I(\bar{h}\bar{k}\bar{l})$. The intensity relationships between the eight octants of three-dimensional data then have only C_2 symmetry, rather than C_{2h} symmetry. Explicitly, we now have $[I(hkl) = I(\bar{h}k\bar{l})] \simeq [I(h\bar{k}l) = I(\bar{h}\bar{k}\bar{l})]$ and $[I(hk\bar{l}) = I(\bar{h}kl)] \simeq [I(h\bar{k}\bar{l}) = I(hkl)]$, where the symbol "$\simeq$" represents a Friedel equality broken by anomalous dispersion. (b) While we have assiduously retained all weak data in our recent studies performed with a four-circle diffractometer [see, for example, M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 2674 (1973)], the errors inherent in the ω-scan technique (*vis a vis* the θ–2θ scan technique) are sufficiently serious as to lead us to reject all data for which $I \leqslant 3[\sigma(I)]$.

(12) CRYM is an integrated sequence of crystallographic routines for the IBM 360 computer, written under the direction of Dr. R. E. Marsh at the California Institute of Technology.

(13) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 202–203.

(14) H. P. Hanson, F. Herman, J. D. Lea, and S. Skellman, *Acta Crystallogr.*, 17, 1040 (1964).

(15) Reference 13, pp 214–215.

(16) The CRYM system allows for the variation of $\Delta f'$ and $\Delta f''$ as a function of $(\sin\theta)/\lambda$.

Table I. Final Parameters for $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$

(A) Positional and Isotropic Thermal Parameter[a]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
Ir(1)	0.09343 (6)	0.06434 (6)	0.14482 (7)		C(68)	0.3647 (22)	0.1261 (16)	0.4888 (26)	5.9 (0.7)
Ir(2)	0.29297 (6)	0	−0.00299 (5)		C(69)	0.2661 (15)	0.0838 (10)	−0.0799 (17)	2.9 (0.4)
Cu(1)	0.19412 (23)	0.11525 (17)	0.00868 (32)		C(70)	0.2490 (17)	0.1331 (12)	−0.1191 (20)	4.0 (0.5)
Cu(2)	0.09516 (23)	0.00563 (17)	−0.04438 (27)		C(71)	0.2431 (19)	0.1805 (13)	−0.1844 (21)	4.7 (0.6)
Cu(3)	0.19434 (24)	−0.04601 (16)	0.13578 (49)		C(72)	0.1786 (21)	0.2260 (15)	−0.1919 (25)	5.6 (0.7)
Cu(4)	0.29095 (23)	0.05684 (20)	0.17830 (27)		C(73)	0.1810 (23)	0.2775 (16)	−0.2584 (28)	6.5 (0.8)
P(1)	−0.02031 (42)	0.09554 (28)	0.21428 (92)		C(74)	0.2401 (21)	0.2826 (14)	−0.3012 (24)	5.4 (0.6)
P(2)	0.39407 (45)	−0.03306 (30)	−0.09061 (51)		C(75)	0.3112 (22)	0.2370 (16)	−0.2959 (25)	5.8 (0.7)
C(1)	−0.1112 (19)	0.0387 (13)	0.2116 (21)	4.3 (0.5)	C(76)	0.3128 (20)	0.1880 (14)	−0.2379 (23)	5.4 (0.7)
C(2)	−0.0848 (21)	−0.0143 (14)	0.2668 (25)	5.6 (0.7)	C(77)	0.1851 (17)	−0.0388 (11)	−0.1044 (19)	3.6 (0.5)
C(3)	−0.1532 (22)	−0.0548 (15)	0.2733 (25)	5.9 (0.7)	C(78)	0.1119 (18)	−0.0559 (13)	−0.1706 (21)	4.4 (0.5)
C(4)	−0.2460 (24)	−0.0477 (16)	0.2036 (28)	6.5 (0.8)	C(79)	0.0494 (20)	−0.0771 (15)	−0.2598 (23)	5.3 (0.6)
C(5)	−0.2640 (22)	−0.0060 (16)	0.1415 (25)	6.1 (0.7)	C(80)	0.0158 (29)	−0.1353 (20)	−0.2547 (34)	8.0 (1.0)
C(6)	−0.1998 (20)	0.0414 (13)	0.1453 (23)	5.0 (0.6)	C(81)	−0.0475 (35)	−0.1578 (25)	−0.3456 (44)	10.7 (1.4)
C(7)	−0.0933 (19)	0.1612 (13)	0.1602 (22)	4.6 (0.6)	C(82)	−0.0747 (30)	−0.1243 (22)	−0.4350 (36)	9.0 (1.1)
C(8)	−0.1368 (22)	0.1914 (16)	0.2134 (27)	6.1 (0.7)	C(83)	−0.0388 (31)	−0.0680 (22)	−0.4319 (36)	8.9 (1.1)
C(9)	−0.2009 (35)	0.2444 (24)	0.1649 (41)	10.6 (1.3)	C(84)	0.0280 (23)	−0.0440 (17)	−0.3421 (28)	6.6 (0.8)
C(10)	−0.2090 (22)	0.2573 (16)	0.0703 (26)	6.3 (0.7)	C(85)	0.3042 (15)	−0.0753 (10)	0.0863 (17)	2.8 (0.4)
C(11)	−0.1607 (21)	0.2234 (15)	0.0082 (24)	5.6 (0.6)	C(86)	0.3042 (19)	−0.1132 (13)	0.1504 (22)	4.7 (0.6)
C(12)	−0.1026 (18)	0.1766 (13)	0.0602 (21)	4.3 (0.5)	C(87)	0.3271 (17)	−0.1601 (12)	0.2248 (19)	3.9 (0.5)
C(13)	0.0209 (17)	0.1197 (12)	0.3496 (19)	4.0 (0.5)	C(88)	0.3571 (22)	−0.2171 (15)	0.1986 (25)	6.0 (0.7)
C(14)	0.0872 (21)	0.1549 (15)	0.3790 (24)	5.5 (0.6)	C(89)	0.3844 (21)	−0.2641 (15)	0.2751 (26)	5.7 (0.7)
C(15)	0.1197 (26)	0.1778 (18)	0.4724 (30)	7.1 (0.9)	C(90)	0.3722 (27)	−0.2559 (19)	0.3583 (30)	7.3 (0.8)
C(16)	0.0832 (27)	0.1582 (19)	0.5438 (31)	7.5 (0.9)	C(91)	0.3359 (23)	−0.2008 (17)	0.3921 (27)	6.6 (0.8)
C(17)	0.0102 (33)	0.1202 (22)	0.5237 (36)	8.8 (1.0)	C(92)	0.3173 (20)	−0.1539 (14)	0.3237 (24)	5.2 (0.6)
C(18)	−0.0327 (25)	0.0993 (18)	0.4180 (30)	7.2 (0.9)	C(93)	0.3902 (22)	0.0430 (15)	0.1119 (26)	6.2 (0.7)
C(19)	0.4874 (15)	0.0150 (11)	−0.0940 (18)	3.8 (0.4)	C(94)	0.4394 (17)	0.0742 (13)	0.1771 (20)	4.6 (0.5)
C(20)	0.4966 (15)	0.0774 (11)	−0.0612 (19)	3.8 (0.5)	C(95)	0.5151 (25)	0.1074 (17)	0.2419 (29)	7.0 (0.8)
C(21)	0.5726 (22)	0.1126 (15)	−0.0658 (26)	6.1 (0.8)	C(96)	0.5002 (33)	0.1645 (24)	0.2740 (40)	9.7 (1.2)
C(22)	0.6436 (18)	0.0871 (13)	−0.1020 (22)	5.1 (0.6)	C(97)	0.5857 (38)	0.1938 (27)	0.3366 (47)	11.8 (1.5)
C(23)	0.6405 (22)	0.0346 (16)	−0.1322 (26)	6.1 (0.7)	C(98)	0.6600 (41)	0.1677 (31)	0.3600 (53)	13.0 (1.8)
C(24)	0.5669 (19)	−0.0072 (14)	−0.1265 (23)	5.1 (0.6)	C(99)	0.6820 (35)	0.1090 (23)	0.3414 (41)	10.1 (1.3)
C(25)	0.4518 (21)	−0.1071 (15)	−0.0404 (24)	5.5 (0.7)	C(100)	0.6022 (38)	0.0768 (30)	0.2754 (46)	12.0 (1.5)
C(26)	0.4578 (28)	−0.1602 (19)	−0.0978 (33)	8.2 (0.9)	H(2)	−0.0212	−0.0222	0.2993	10.0
C(27)	0.5120 (25)	−0.2083 (17)	−0.0289 (30)	7.7 (0.9)	H(3)	−0.1406	−0.0868	0.3218	10.0
C(28)	0.5569 (32)	−0.2060 (27)	0.0513 (39)	10.5 (1.3)	H(4)	−0.2935	−0.0760	0.2064	10.0
C(29)	0.5484 (29)	−0.1556 (20)	0.1044 (34)	8.6 (1.0)	H(5)	−0.3215	−0.0059	0.0907	10.0
C(30)	0.5003 (26)	−0.1043 (18)	0.0582 (30)	7.4 (0.8)	H(6)	−0.2172	0.0756	0.1021	10.0
C(31)	0.3474 (24)	−0.0470 (16)	−0.2264 (28)	6.7 (0.8)	H(8)	−0.1297	0.1813	0.2828	10.0
C(32)	0.3534 (37)	−0.0137 (27)	−0.2959 (46)	11.9 (1.5)	H(9)	−0.2338	0.2672	0.2037	10.0
C(33)	0.3078 (43)	−0.0228 (30)	−0.4027 (55)	14.3 (1.9)	H(10)	−0.2480	0.2901	0.0404	10.0
C(34)	0.2673 (49)	−0.0699 (34)	−0.4245 (60)	16.0 (2.2)	H(11)	−0.1676	0.2320	−0.0618	10.0
C(35)	0.2456 (33)	−0.1092 (23)	−0.3523 (43)	10.2 (1.2)	H(12)	−0.0674	0.1541	0.0235	10.0
C(36)	0.2835 (26)	−0.0971 (19)	−0.2414 (31)	7.2 (0.8)	H(14)	0.1186	0.1671	0.3297	10.0
C(37)	0.1125 (18)	0.1492 (12)	0.0983 (20)	4.2 (0.5)	H(15)	0.1678	0.2074	0.4863	10.0
C(38)	0.1436 (19)	0.1936 (13)	0.0713 (21)	4.8 (0.6)	H(16)	0.1090	0.1711	0.6118	10.0
C(39)	0.1538 (15)	0.2617 (10)	0.0498 (17)	3.3 (0.5)	H(17)	−0.0145	0.1065	0.5775	10.0
C(40)	0.0828 (27)	0.3006 (19)	0.0462 (31)	7.6 (0.9)	H(18)	−0.0880	0.0758	0.3981	10.0
C(41)	0.0809 (32)	0.3619 (22)	0.0250 (36)	8.8 (1.0)	H(20)	0.4489	0.0950	−0.0355	10.0
C(42)	0.1574 (30)	0.3835 (21)	0.0104 (36)	8.5 (1.0)	H(21)	0.5763	0.1538	−0.0444	10.0
C(43)	0.2432 (34)	0.3483 (22)	0.0196 (40)	9.4 (1.1)	H(22)	0.6962	0.1113	−0.1032	10.0
C(44)	0.2283 (25)	0.2830 (19)	0.0404 (30)	7.2 (0.9)	H(23)	0.6887	0.0207	−0.1607	10.0
C(45)	0.0001 (20)	0.0489 (12)	0.0056 (22)	4.4 (0.5)	H(24)	0.5706	−0.0488	−0.1438	10.0
C(46)	−0.0476 (16)	0.0390 (10)	−0.0791 (17)	3.1 (0.4)	H(26)	0.4316	−0.1645	−0.1689	10.0
C(47)	−0.1147 (20)	0.0434 (13)	−0.1790 (23)	4.9 (0.6)	H(27)	0.5075	−0.2476	−0.0585	10.0
C(48)	−0.1409 (26)	0.0934 (17)	−0.2199 (29)	7.2 (0.8)	H(28)	0.5986	−0.2378	0.0801	10.0
C(49)	−0.2015 (34)	0.1018 (25)	−0.3185 (41)	10.2 (1.3)	H(29)	0.5760	−0.1549	0.1756	10.0
C(50)	−0.2317 (25)	0.0492 (16)	−0.3621 (31)	7.1 (0.9)	H(30)	0.5017	−0.0678	0.0957	10.0
C(51)	−0.2117 (27)	−0.0047 (20)	−0.3272 (30)	7.8 (0.9)	H(32)	0.3914	0.0214	−0.2786	10.0
C(52)	−0.1472 (24)	−0.0097 (17)	−0.2283 (28)	6.6 (0.7)	H(33)	0.3098	0.0069	−0.4526	10.0
C(53)	0.0902 (17)	−0.0228 (12)	0.1798 (19)	3.5 (0.5)	H(34)	0.2489	−0.0814	−0.4941	10.0
C(54)	0.0962 (16)	−0.0758 (11)	0.2208 (19)	3.5 (0.5)	H(35)	0.2067	−0.1435	−0.3743	10.0
C(55)	0.0886 (21)	−0.1317 (15)	0.2607 (26)	5.5 (0.6)	H(36)	0.2677	−0.1193	−0.1884	10.0
C(56)	0.0773 (22)	−0.1880 (16)	0.2083 (25)	6.0 (0.7)	H(40)	0.0283	0.2840	0.0597	10.0
C(57)	0.0766 (28)	−0.2431 (19)	0.2442 (33)	8.4 (0.9)	H(41)	0.0275	0.3864	0.0214	10.0
C(58)	0.0776 (30)	−0.2451 (22)	0.3456 (37)	9.5 (1.1)	H(42)	0.1581	0.4252	−0.0076	10.0
C(59)	0.0746 (35)	−0.1977 (27)	0.4014 (42)	10.8 (1.4)	H(43)	0.3004	0.3649	0.0133	10.0
C(60)	0.0833 (28)	−0.1379 (20)	0.3520 (35)	8.3 (1.0)	H(44)	0.2794	0.2560	0.0468	10.0
C(61)	0.2032 (15)	0.0734 (11)	0.2716 (17)	3.2 (0.4)	H(48)	−0.1183	0.1288	−0.1817	10.0
C(62)	0.2807 (15)	0.0723 (11)	0.3317 (17)	3.3 (0.4)	H(49)	−0.2182	0.1403	−0.3493	10.0
C(63)	0.3591 (16)	0.0810 (11)	0.4159 (17)	3.4 (0.5)	H(50)	−0.2737	0.0517	−0.4277	10.0
C(64)	0.4289 (23)	0.0365 (16)	0.4292 (28)	6.4 (0.7)	H(51)	−0.2382	−0.0396	−0.3648	10.0
C(65)	0.5074 (27)	0.0377 (17)	0.5144 (32)	7.2 (0.8)	H(52)	−0.1279	−0.0480	−0.1985	10.0
C(66)	0.5100 (25)	0.0866 (18)	0.5939 (29)	7.5 (0.9)	H(56)	0.0689	−0.1853	0.1368	10.0
C(67)	0.4406 (33)	0.1227 (24)	0.5792 (42)	10.1 (1.2)	H(57)	0.0756	−0.2785	0.2040	10.0

Table I *(Continued)*

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(58)	0.0807	−0.2839	0.3770	10.0	H(81)	−0.0721	−0.1975	−0.3447	10.0
H(59)	0.0674	−0.2006	0.4685	10.0	H(82)	−0.1161	−0.1401	−0.4947	10.0
H(60)	0.0849	−0.1022	0.3915	10.0	H(83)	−0.0576	−0.0430	−0.4904	10.0
H(64)	0.4234	0.0051	0.3803	10.0	H(84)	0.0552	−0.0051	−0.3436	10.0
H(65)	0.5564	0.0091	0.5217	10.0	H(88)	0.3858	−0.1925	0.1582	10.0
H(66)	0.5613	0.0901	0.6521	10.0	H(89)	0.4115	−0.3008	0.2599	10.0
H(67)	0.4389	0.1498	0.6329	10.0	H(90)	0.3877	−0.2882	0.4058	10.0
H(68)	0.3201	0.1579	0.4792	10.0	H(91)	0.3256	−0.1974	0.4579	10.0
H(72)	0.1331	0.2240	−0.1542	10.0	H(92)	0.2971	−0.1161	0.3441	10.0
H(73)	0.1338	0.3076	−0.2675	10.0	H(96)	0.4408	0.1835	0.2576	10.0
H(74)	0.2412	0.3181	−0.3407	10.0	H(97)	0.5822	0.2344	0.3591	10.0
H(75)	0.3564	0.2419	−0.3334	10.0	H(98)	0.7108	0.1914	0.3970	10.0
H(76)	0.3601	0.1582	−0.2325	10.0	H(99)	0.7417	0.0913	0.3679	10.0
H(80)	0.0336	−0.1591	−0.1946	10.0	H(100)	0.6086	0.0361	0.2554	10.0

(B) Anisotropic Thermal Parameters ($\times 10^5$) for Iridium, Copper, and Phosphorus Atoms[a,b]

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	347 (5)	141 (2)	539 (6)	10 (6)	112 (9)	−27 (6)
Ir(2)	360 (5)	158 (2)	537 (6)	22 (5)	120 (8)	−46 (8)
Cu(1)	482 (19)	203 (9)	561 (22)	27 (20)	222 (32)	−2 (23)
Cu(2)	420 (17)	198 (8)	762 (22)	34 (21)	323 (30)	−61 (26)
Cu(3)	482 (21)	180 (9)	727 (24)	98 (19)	247 (34)	61 (24)
Cu(4)	469 (16)	229 (8)	634 (21)	59 (21)	294 (35)	−103 (24)
P(1)	337 (28)	125 (13)	586 (43)	55 (34)	37 (56)	−100 (38)
P(2)	429 (33)	172 (17)	645 (41)	23 (34)	329 (56)	−159 (50)

(C) Axes of Thermal Vibration Ellipsoids (Å^2)[c]

	B (direction cosines)		
Atom	Major axis	Median axis	Minor axis
Ir(1)	4.07	2.76	2.70
	(−0.501, −0.140, 0.955)	(0.820, 0.239, 0.290)	(−0.277, 0.961, 0.067)
Ir(2)	4.15	2.96	2.84
	(0.512, 0.299, −0.910)	(−0.146, −0.893, −0.373)	(−0.846, 0.336, −0.180)
Cu(1)	4.25	3.88	3.73
	(−0.798, −0.465, 0.577)	(0.113, −0.741, −0.699)	(−0.592, 0.485, −0.468)
Cu(2)	5.37	3.90	3.24
	(−0.116, −0.251, 0.958)	(−0.460, −0.844, −0.147)	(−0.880, 0.474, 0.245)
Cu(3)	5.17	4.39	3.05
	(0.286, −0.107, −0.994)	(−0.807, −0.564, 0.037)	(−0.518, 0.819, −0.104)
Cu(4)	5.15	4.10	3.41
	(−0.322, −0.742, 0.651)	(0.598, 0.322, 0.554)	(0.734, −0.588, −0.519)
P(1)	4.90	2.61	2.15
	(−0.530, −0.299, 0.904)	(−0.765, −0.237, −0.380)	(0.367, −0.925, −0.195)
P(2)	4.98	3.60	2.62
	(−0.078, −0.501, 0.853)	(0.894, 0.347, 0.042)	(0.441, −0.793, −0.521)

[a] Estimated standard deviations are shown in parentheses; they are right adjusted to the least significant digit of the preceding number. [b] The anisotropic thermal parameter is defined as $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. [c] The major, median, and minor axes of the atomic thermal vibration ellipsoids are defined in terms of the isotropic thermal parameter B, since this is a unit familiar to most crystallographers. The transformation to root-mean-square displacement is $\langle \bar{U}^2\rangle^{1/2} = [B/8\pi^2]^{1/2}$.

A Fourier synthesis, phased by the six metal atoms ($R_F = 25.6\%$) revealed only the locations of the two phosphorus atoms. Four cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of the eight "heavy" atoms led to a reduced discrepancy index of $R_F = 19.3\%$. An "observed" Fourier synthesis at this stage of refinement yielded the locations of no additional atoms; somewhat surprisingly, however, a corresponding difference-Fourier synthesis led to the unequivocal location of 92 of the 100 carbon atoms. A second difference-Fourier synthesis ($R_F = 15.6\%$) revealed the remaining eight nonhydrogen atoms.

Two cycles of refinement of the overall scale factor and positional and isotropic thermal parameters for all heavy atoms (with carbon atoms fixed in their observed positions and each assigned a thermal parameter of 5.0 Å^2) led to $R_F = 13.3\%$. Six cycles of refinement of positional and isotropic thermal parameters for all 108 nonhydrogen atoms (with parameters blocked into 11 submatrices, one of which contained the scale factor and all parameters for the eight heavy atoms) led to convergence at $R_F = 10.2\%$. At this stage hydrogen atoms were included in calculated positions with their isotropic thermal parameters set at 10.0 Å^2. The hydrogen atom positional parameters were not refined but, after each cycle, were redefined to be consistent with the updated carbon atom locations. A further 12 cycles of refinement of all positional parameters, isotropic thermal parameters for carbon atoms, and anisotropic thermal parameters for iridium, copper, and phosphorus atoms led to convergence (as defined by $(\Delta/\sigma)_{\max} < 0.25$) with $R_F = 8.2\%$. Reversal of the sign of all y coordinates led to the increased discrepancy index, $R_F = 8.5\%$. Clearly, the polarity of the crystal was that defined by the former set of coordinates.

A final difference-Fourier synthesis showed no residual electron density greater than 1 e Å^{-3} save in the immediate vicinity of some of the heavy atoms. The structure was therefore judged to be both correct and complete.

A table of observed and calculated structure factor amplitudes is available elsewhere.[17] The final atomic positional and thermal parameters are listed in Table I.

The Crystallographically Determined Structure

Interatomic distances and their estimated standard deviations (esd's) are collected in Table II; bond angles (with esd's) are listed in Table III. Important least-squares planes are given in Table IV, while dihedral angles are shown in Table V.

Thermal ellipsoids for the atoms of the $Cu_4Ir_2P_2$ "core" of the molecule are shown in Figure 1. The overall geometry of the $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ molecule is illustrated in

[17] See paragraph at end of paper regarding supplementary material.

Table II. Bond Distances (Å) within the $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$ Molecule

Atoms	Dist	Atoms	Dist
	(A) Iridium–Copper Distances		
Ir(1)–Cu(1)	2.894 (4)	Ir(2)–Cu(1)	2.959 (4)
Ir(1)–Cu(2)	2.890 (4)	Ir(2)–Cu(2)	2.848 (4)
Ir(1)–Cu(3)	2.877 (4)	Ir(2)–Cu(3)	2.861 (5)
Ir(1)–Cu(4)	2.856 (4)	Ir(2)–Cu(4)	2.776 (4)
		Ir–Cu (av)	2.870 (51)[a]
	(B) Copper–Copper Distances		
Cu(1)–Cu(2)	2.823 (5)	Cu(3)–Cu(4)	2.665 (6)
Cu(2)–Cu(3)	2.759 (7)	Cu(4)–Cu(1)	2.709 (6)
		Cu–Cu (av)	2.739 (68)[a]
	(C) Iridium–Phosphorus Distances		
Ir(1)–P(1)	2.248 (8)	Ir(2)–P(2)	2.268 (7)
		Ir–P (av)	2.258 (14)[a]
	(D) Iridium–Acetylene C(α) Distances		
Ir(1)–C(37)	2.018 (27)	Ir(2)–C(69)	2.109 (21)
Ir(1)–C(45)	2.067 (29)	Ir(2)–C(77)	2.015 (25)
Ir(1)–C(53)	1.982 (26)	Ir(2)–C(85)	2.039 (22)
Ir(1)–C(61)	2.055 (23)	Ir(2)–C(93)	2.064 (34)
		Ir–C (av)	2.044 (39)[a]
	(E) Copper–Acetylene C(α) Distances		
Cu(1)–C(37)	2.071 (28)	Cu(1)–C(69)	1.936 (23)
Cu(2)–C(45)	1.966 (29)	Cu(2)–C(77)	1.995 (25)
Cu(3)–C(53)	1.871 (26)	Cu(3)–C(85)	2.027 (23)
Cu(4)–C(61)	2.076 (23)	Cu(4)–C(93)	1.944 (34)
		Cu–C(α) (av)	1.986 (70)[a]
	(F) Copper–Acetylene C(β) Distances		
Cu(1)–C(38)	2.145 (29)	Cu(1)–C(70)	2.142 (26)
Cu(2)–C(46)	2.178 (24)	Cu(2)–C(78)	2.254 (28)
Cu(3)–C(54)	2.186 (25)	Cu(3)–C(86)	2.174 (29)
Cu(4)–C(62)	2.161 (22)	Cu(4)–C(94)	2.243 (27)
		Cu–C(β) (av)	2.185 (42)[a]
	(G) Acetylene C(α)–C(β) Distances		
C(37)–C(38)	1.181 (39)	C(69)–C(70)	1.209 (34)
C(45)–C(46)	1.207 (37)	C(77)–C(78)	1.277 (37)
C(53)–C(54)	1.289 (35)	C(85)–C(86)	1.208 (36)
C(61)–C(62)	1.227 (32)	C(93)–C(94)	1.209 (43)
		C≡C (av)	1.226 (37)[a]
	(H) Acetylene C(β)–Phenyl Distances		
C(38)–C(39)	1.545 (37)	C(70)–C(71)	1.360 (38)
C(46)–C(47)	1.466 (38)	C(78)–C(79)	1.403 (41)
C(54)–C(55)	1.362 (40)	C(86)–C(87)	1.426 (38)
C(62)–C(63)	1.421 (32)	C(94)–C(95)	1.437 (47)
		C(β)–phenyl (av)	1.428 (60)[a]
	(I) Phosphorus–Phenyl Distances		
P(1)–C(1)	1.836 (30)	P(2)–C(19)	1.756 (24)
P(1)–C(7)	1.844 (30)	P(2)–C(25)	1.888 (33)
P(1)–C(13)	1.863 (28)	P(2)–C(31)	1.824 (38)
		P–phenyl (av)	1.835 (46)[a]

Atoms	Dist	Atoms	Dist
	(J) Carbon–Carbon Distances within the Phenyl Rings		
C(1)–C(2)	1.389 (42)	C(19)–C(20)	1.441 (33)
C(2)–C(3)	1.373 (46)	C(20)–C(21)	1.385 (41)
C(3)–C(4)	1.466 (50)	C(21)–C(22)	1.393 (44)
C(4)–C(5)	1.230 (50)	C(22)–C(23)	1.224 (45)
C(5)–C(6)	1.407 (46)	C(23)–C(24)	1.449 (46)
C(6)–C(1)	1.391 (42)	C(24)–C(19)	1.450 (38)
C(7)–C(8)	1.277 (45)	C(25)–C(26)	1.421 (53)
C(8)–C(9)	1.544 (64)	C(26)–C(27)	1.504 (57)
C(9)–C(10)	1.294 (64)	C(27)–C(28)	1.123 (65)
C(10)–C(11)	1.451 (47)	C(28)–C(29)	1.351 (72)
C(11)–C(12)	1.412 (42)	C(29)–C(30)	1.396 (59)
C(12)–C(7)	1.376 (40)	C(30)–C(25)	1.351 (51)
C(13)–C(14)	1.237 (41)	C(31)–C(32)	1.220 (71)
C(14)–C(15)	1.336 (51)	C(32)–C(33)	1.451 (94)
C(15)–C(16)	1.304 (57)	C(33)–C(34)	1.197 (102)
C(16)–C(17)	1.341 (64)	C(34)–C(35)	1.410 (94)
C(17)–C(18)	1.488 (62)	C(35)–C(36)	1.494 (69)
C(18)–C(13)	1.444 (47)	C(36)–C(31)	1.436 (55)
C(39)–C(40)	1.350 (48)	C(71)–C(72)	1.373 (43)
C(40)–C(41)	1.380 (64)	C(72)–C(73)	1.458 (49)
C(41)–C(42)	1.295 (67)	C(73)–C(74)	1.180 (48)
C(42)–C(43)	1.469 (69)	C(74)–C(75)	1.447 (47)
C(43)–C(44)	1.495 (64)	C(75)–C(76)	1.335 (46)
C(44)–C(39)	1.240 (46)	C(76)–C(71)	1.422 (42)
C(47)–C(48)	1.249 (47)	C(79)–C(80)	1.386 (55)
C(48)–C(49)	1.422 (66)	C(80)–C(81)	1.434 (72)
C(49)–C(50)	1.327 (66)	C(81)–C(82)	1.392 (74)
C(50)–C(51)	1.285 (56)	C(82)–C(83)	1.345 (69)
C(51)–C(52)	1.441 (55)	C(83)–C(84)	1.459 (61)
C(52)–C(47)	1.373 (48)	C(84)–C(79)	1.306 (49)
C(55)–C(56)	1.419 (47)	C(87)–C(88)	1.408 (42)
C(56)–C(57)	1.312 (55)	C(88)–C(89)	1.451 (47)
C(57)–C(58)	1.378 (65)	C(89)–C(90)	1.208 (52)
C(58)–C(59)	1.301 (75)	C(90)–C(91)	1.451 (55)
C(59)–C(60)	1.501 (73)	C(91)–C(92)	1.371 (48)
C(60)–C(55)	1.273 (56)	C(92)–C(87)	1.400 (40)
C(63)–C(64)	1.405 (43)	C(95)–C(96)	1.369 (65)
C(64)–C(65)	1.416 (55)	C(96)–C(97)	1.482 (79)
C(65)–C(66)	1.520 (56)	C(97)–C(98)	1.212 (88)
C(66)–C(67)	1.277 (65)	C(98)–C(99)	1.374 (84)
C(67)–C(68)	1.441 (64)	C(99)–C(100)	1.471 (81)
C(68)–C(63)	1.391 (41)	C(100)–C(95)	1.426 (72)
		Phenyl C–C (av)	1.376 (91)[a]

[a] Esd's on average bond lengths are calculated from the expression

$$\sigma = \{[\sum_{N=1}^{i=N} (X_i - \bar{X})]/(N-1)\}^{1/2}$$

where X_i is the ith bond length and $\bar{X}$ is the mean of N equivalent bond lengths.

Figure 2, while essential details of the atomic numbering scheme are shown in Figure 3. [Within the phenylethynyl ligands, the phenyl carbons are labeled cyclically as C(n + 1) through C(n + 6), where C(n + 1) is bonded directly to the β-acetylenic carbon designated C(n). Phenyl groups within the triphenylphosphine ligand are again numbered cyclically, with C(1), C(7), and C(13) being bonded directly to P(1) and with C(19), C(25), and C(31) being linked to P(2). Hydrogen atoms are numbered similarly to their attached carbon atoms.]

As shown clearly in the figures, the six metal atoms define a slightly irregular octahedron in which the two iridium atoms are mutually trans. One triphenylphosphine ligand is bonded apically to each iridium atom and four phenylethynyl ligands are σ bonded to each iridium atom in such a manner that two phenylethynyl units (one associated with each iridium atom) form unsymmetrical π linkages to each of the four equatorial copper atoms. The formal oxidation states of the metal atoms are therefore Cu(0) and Ir(IV).[18-20]

(18) Formal oxidation state is defined as the net electronic charge remaining on the metal atom after all the ligands have been removed in their closed-shell configurations. In the present molecule the phenylethynyl ligands are considered to be present as $Ph-C{\equiv}C^-$; removal of four of these ligands (and one PPh_3 ligand) from each iridium atom thus leaves the iridium in a +4 oxidation state. Formal oxidation state should not be confused with the actual charge residing on a metal atom when all the ligands are still bonded to it. An *actual* charge of 4+ on the iridium atom would be in violation of the Pauling electroneutrality principle.[19] One would, however, predict some small partial positive charge on iridium, since the electronegativity[20] of carbon is 2.55 as compared to a value of

Table III. Angles (deg) within the $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$ Molecule

Atoms	Angle	Atoms	Angle
(A) Angles in Triangular Faces of the Cu_4Ir_2 Octahedron			
Cu(1)-Ir(1)-Cu(2)	58.4 (1)	Ir(1)-Cu(2)-Cu(1)	60.9 (1)
Cu(2)-Ir(1)-Cu(3)	57.2 (1)	Ir(1)-Cu(2)-Cu(3)	61.1 (1)
Cu(3)-Ir(1)-Cu(4)	55.4 (1)	Ir(2)-Cu(2)-Cu(1)	62.9 (1)
Cu(4)-Ir(1)-Cu(1)	56.2 (1)	Ir(2)-Cu(2)-Cu(3)	61.3 (1)
Cu(1)-Ir(2)-Cu(2)	58.1 (1)	Ir(1)-Cu(3)-Cu(2)	61.7 (1)
Cu(2)-Ir(2)-Cu(3)	57.8 (1)	Ir(1)-Cu(3)-Cu(4)	61.9 (1)
Cu(3)-Ir(2)-Cu(4)	56.4 (1)	Ir(2)-Cu(3)-Cu(2)	60.9 (1)
Cu(4)-Ir(2)-Cu(1)	56.3 (1)	Ir(2)-Cu(3)-Cu(4)	60.2 (1)
Ir(1)-Cu(1)-Cu(2)	60.7 (1)	Ir(1)-Cu(4)-Cu(1)	62.6 (1)
Ir(1)-Cu(1)-Cu(4)	61.2 (1)	Ir(1)-Cu(4)-Cu(3)	62.7 (1)
Ir(2)-Cu(1)-Cu(2)	59.0 (1)	Ir(2)-Cu(4)-Cu(1)	65.3 (1)
Ir(2)-Cu(1)-Cu(4)	58.4 (1)	Ir(2)-Cu(4)-Cu(3)	63.4 (2)
(B) Angles in Rhombohedral Planes of the Cu_4Ir_2 Octahedron			
Cu(1)-Ir(1)-Cu(3)	86.5 (1)	Ir(1)-Cu(2)-Ir(2)	95.2 (1)
Cu(2)-Ir(1)-Cu(4)	82.5 (1)	Cu(1)-Cu(2)-Cu(3)	90.2 (2)
Cu(1)-Ir(2)-Cu(3)	85.5 (1)	Ir(1)-Cu(3)-Ir(2)	95.2 (1)
Cu(2)-Ir(2)-Cu(4)	84.7 (1)	Cu(2)-Cu(3)-Cu(4)	88.6 (2)
Ir(1)-Cu(1)-Ir(2)	92.8 (1)	Ir(1)-Cu(4)-Ir(2)	97.6 (1)
Cu(2)-Cu(1)-Cu(4)	86.4 (2)	Cu(1)-Cu(4)-Cu(3)	94.7 (2)
(C) Phosphorus-Iridium-Iridium Angles			
P(1)-Ir(1)-Ir(2)	175.9 (3)	P(2)-Ir(2)-Ir(1)	176.8 (2)
(D) Phosphorus-Iridium-Copper Angles			
P(1)-Ir(1)-Cu(1)	136.1 (2)	P(2)-Ir(2)-Cu(1)	135.2 (2)
P(1)-Ir(1)-Cu(2)	133.9 (3)	P(2)-Ir(2)-Cu(2)	134.5 (2)
P(1)-Ir(1)-Cu(3)	137.2 (2)	P(2)-Ir(2)-Cu(3)	139.2 (2)
P(1)-Ir(1)-Cu(4)	143.5 (3)	P(2)-Ir(2)-Cu(4)	140.8 (2)
(E) Phosphorus-Iridium-Acetylene C(α) Angles			
P(1)-Ir(1)-C(37)	91.8 (8)	P(2)-Ir(2)-C(69)	94.9 (6)
P(1)-Ir(1)-C(45)	92.2 (9)	P(2)-Ir(2)-C(77)	91.2 (7)
P(1)-Ir(1)-C(53)	97.3 (8)	P(2)-Ir(2)-C(85)	95.1 (7)
P(1)-Ir(1)-C(61)	97.8 (7)	P(2)-Ir(2)-C(93)	96.7 (10)
(F) Acetylene C(α)-Iridium-Acetylene C(α) Angles			
C(37)-Ir(1)-C(45)	88.9 (11)	C(69)-Ir(2)-C(77)	90.9 (9)
C(45)-Ir(1)-C(53)	90.4 (10)	C(77)-Ir(2)-C(85)	89.5 (9)
C(53)-Ir(1)-C(61)	87.5 (10)	C(85)-Ir(2)-C(93)	89.4 (11)
C(61)-Ir(1)-C(37)	91.6 (10)	C(93)-Ir(2)-C(69)	88.8 (11)
(G) Iridium-C(α)-C(β) Angles			
Ir(1)-C(37)-C(38)	164.5 (25)	Ir(2)-C(69)-C(70)	176.2 (20)
Ir(1)-C(45)-C(46)	174.2 (25)	Ir(2)-C(77)-C(78)	172.0 (22)
Ir(1)-C(53)-C(54)	168.5 (21)	Ir(2)-C(85)-C(86)	168.1 (21)
Ir(1)-C(61)-C(62)	164.0 (20)	Ir(2)-C(93)-C(94)	171.8 (28)
		Ir-C(α)-C(β) (av)	169.9 ± 4.4
(H) C(α)-C(β)-Phenyl Angles			
C(37)-C(38)-C(39)	158.4 (29)	C(69)-C(70)-C(71)	161.9 (28)
C(45)-C(46)-C(47)	164.6 (26)	C(77)-C(78)-C(79)	163.8 (29)
C(53)-C(54)-C(55)	171.6 (28)	C(85)-C(86)-C(87)	165.9 (29)
C(61)-C(62)-C(63)	165.2 (25)	C(93)-C(94)-C(95)	165.9 (32)
		C(α)-C(β)-phenyl (av)	164.7 ± 3.8
(I) Copper-C(α)-C(β) Angles			
Cu(1)-C(37)-C(38)	77.2 (20)	Cu(1)-C(69)-C(70)	82.4 (17)
Cu(2)-C(45)-C(46)	83.0 (19)	Cu(2)-C(77)-C(78)	84.0 (18)
Cu(3)-C(53)-C(54)	85.4 (17)	Cu(3)-C(85)-C(86)	80.1 (18)
Cu(4)-C(61)-C(62)	77.0 (15)	Cu(4)-C(93)-C(94)	87.5 (22)
(J) Copper-C(β)-C(α) Angles			
Cu(1)-C(38)-C(37)	70.3 (19)	Cu(1)-C(70)-C(69)	63.6 (15)
Cu(2)-C(46)-C(45)	63.6 (17)	Cu(2)-C(78)-C(77)	61.7 (16)
Cu(3)-C(54)-C(53)	58.6 (15)	Cu(3)-C(86)-C(85)	66.7 (17)
Cu(4)-C(62)-C(61)	69.4 (14)	Cu(4)-C(94)-C(93)	60.0 (20)
(K) C(α)-Copper-C(β) Angles			
C(37)-Cu(1)-C(38)	32.5 (11)	C(69)-Cu(1)-C(70)	34.0 (9)
C(45)-Cu(2)-C(46)	33.4 (10)	C(77)-Cu(2)-C(78)	34.3 (10)
C(53)-Cu(3)-C(54)	36.0 (10)	C(85)-Cu(3)-C(86)	33.2 (10)
C(61)-Cu(4)-C(62)	33.6 (9)	C(93)-Cu(4)-C(94)	32.6 (12)
(L) Iridium-Phosphorus-Carbon Angles			
Ir(1)-P(1)-C(1)	114.4 (10)	Ir(2)-P(2)-C(19)	117.1 (8)
Ir(1)-P(1)-C(7)	120.0 (10)	Ir(2)-P(2)-C(25)	112.9 (10)
Ir(1)-P(1)-C(13)	114.4 (9)	Ir(2)-P(2)-C(31)	117.2 (12)
(M) Carbon-Phosphorus-Carbon Angles			
C(1)-P(1)-C(7)	100.0 (13)	C(19)-P(2)-C(25)	104.1 (13)
C(7)-P(1)-C(13)	100.4 (12)	C(25)-P(2)-C(31)	103.8 (15)
C(13)-P(1)-C(1)	105.4 (13)	C(31)-P(2)-C(19)	99.8 (14)
(N) Carbon-Carbon-Carbon Angles within the Phenyl Rings			
C(1)-C(2)-C(3)	118.2 (29)	C(13)-C(14)-C(15)	127.3 (33)
C(2)-C(3)-C(4)	118.4 (30)	C(14)-C(15)-C(16)	117.9 (37)
C(3)-C(4)-C(5)	121.7 (34)	C(15)-C(16)-C(17)	121.7 (41)
C(4)-C(5)-C(6)	120.4 (33)	C(16)-C(17)-C(18)	120.7 (41)
C(5)-C(6)-C(1)	120.7 (27)	C(17)-C(18)-C(13)	111.0 (33)
C(6)-C(1)-C(2)	118.3 (27)	C(18)-C(13)-C(14)	120.8 (28)
C(7)-C(8)-C(9)	119.9 (35)	C(19)-C(20)-C(21)	122.2 (24)
C(8)-C(9)-C(10)	118.6 (43)	C(20)-C(21)-C(22)	119.4 (28)
C(9)-C(10)-C(11)	122.4 (37)	C(21)-C(22)-C(23)	122.3 (30)
C(10)-C(11)-C(12)	114.5 (28)	C(22)-C(23)-C(24)	123.1 (31)
C(11)-C(12)-C(7)	124.6 (27)	C(23)-C(24)-C(19)	119.1 (27)
C(12)-C(7)-C(8)	119.9 (29)	C(24)-C(19)-C(20)	113.5 (22)
C(25)-C(26)-C(27)	109.6 (34)	C(55)-C(56)-C(57)	129.3 (34)
C(26)-C(27)-C(28)	131.5 (46)	C(56)-C(57)-C(58)	113.9 (39)
C(27)-C(28)-C(29)	116.3 (51)	C(57)-C(58)-C(59)	124.5 (47)
C(28)-C(29)-C(30)	122.2 (43)	C(58)-C(59)-C(60)	115.1 (47)
C(29)-C(30)-C(25)	119.3 (36)	C(59)-C(60)-C(55)	124.5 (42)
C(30)-C(25)-C(26)	119.4 (33)	C(60)-C(55)-C(56)	111.6 (33)
C(31)-C(32)-C(33)	125.8 (56)	C(63)-C(64)-C(65)	121.1 (31)
C(32)-C(33)-C(34)	116.3 (69)	C(64)-C(65)-C(66)	117.4 (34)
C(33)-C(34)-C(35)	123.4 (74)	C(65)-C(66)-C(67)	117.4 (40)
C(34)-C(35)-C(36)	120.1 (50)	C(66)-C(67)-C(68)	126.0 (46)
C(35)-C(36)-C(31)	110.1 (36)	C(67)-C(68)-C(63)	117.5 (33)
C(36)-C(31)-C(32)	122.1 (43)	C(68)-C(63)-C(64)	120.1 (26)
C(39)-C(40)-C(41)	127.1 (39)	C(71)-C(72)-C(73)	119.1 (29)
C(40)-C(41)-C(42)	114.9 (44)	C(72)-C(73)-C(74)	121.5 (34)
C(41)-C(42)-C(43)	124.7 (45)	C(73)-C(74)-C(75)	122.5 (33)
C(42)-C(43)-C(44)	111.0 (40)	C(74)-C(75)-C(76)	119.5 (30)
C(43)-C(44)-C(39)	124.3 (37)	C(75)-C(76)-C(71)	119.6 (29)
C(44)-C(39)-C(40)	117.8 (31)	C(76)-C(71)-C(72)	117.7 (27)
C(47)-C(48)-C(49)	125.8 (39)	C(79)-C(80)-C(81)	116.2 (40)
C(48)-C(49)-C(50)	111.4 (44)	C(80)-C(81)-C(82)	123.3 (47)
C(49)-C(50)-C(51)	128.6 (43)	C(81)-C(82)-C(83)	116.0 (46)
C(50)-C(51)-C(52)	116.7 (38)	C(82)-C(83)-C(84)	122.6 (43)
C(51)-C(52)-C(47)	117.2 (34)	C(83)-C(84)-C(79)	118.6 (35)
C(52)-C(47)-C(48)	120.2 (33)	C(84)-C(79)-C(80)	123.3 (34)
C(87)-C(88)-C(89)	120.2 (28)	C(95)-C(96)-C(97)	113.5 (44)
C(88)-C(89)-C(90)	118.9 (34)	C(96)-C(97)-C(98)	122.0 (59)
C(89)-C(90)-C(91)	125.7 (38)	C(97)-C(98)-C(99)	130.1 (65)
C(90)-C(91)-C(92)	116.2 (32)	C(98)-C(99)-C(100)	111.9 (52)
C(91)-C(92)-C(87)	121.8 (29)	C(99)-C(100)-C(95)	119.2 (51)
C(92)-C(87)-C(88)	116.8 (26)	C(100)-C(95)-C(96)	122.8 (43)

Individual iridium-copper distances range from 2.776 (4) to 2.959 (4) Å, the average value being 2.870 ± 0.051 Å.[21] Copper-copper distances range from 2.665 (6) to 2.823 (5) Å, averaging 2.739 ± 0.068 Å.

The triphenylphosphine-iridium bond distances are Ir(1)-P(1) = 2.248 (8) Å and Ir(2)-P(2) = 2.268 (7) Å. The average value of 2.258 ± 0.014 Å is significantly shorter than iridium-phosphorus distances previously reported[22-45] in

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2.20 for iridium. The phosphine ligand will have little effect since the electronegativity of phosphorus is 2.19.

(19) L. Pauling "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 172 ff.

(20) These are "Pauling-like" values, taken from A. L. Allred, *J. Inorg. Nucl. Chem.*, 17, 215 (1961).

(21) Throughout the text esd's on individual bond distances and angles are shown in parentheses. Deviations on average values are shown as ±*X.XXX* Å, and are calculated *via* the "root-mean-square scatter" formula shown in footnote *a* to Table II. When the scatter is appreciably larger than the individual esd's, then there is some real difference in the individual bond distances or angles.

(22) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 91, 6301 (1969).

Table IV. Least-Squares Planes within the $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$ Molecule[a,b]

Atom	Dev, Å	Atom	Dev, Å
A. $0.1220X + 0.8933Y - 0.4326Z = 0.552$			
Ir(1)	−0.003	Cu(4)	+0.003
Ir(2)	−0.003	P(1)*	−0.020
Cu(2)	+0.003	P(2)*	+0.066
B. $0.5542X + 0.2962Y + 0.7779Z = 2.405$			
Ir(1)	−0.018	Cu(3)	0.018
Ir(2)	−0.018	P(1)*	−0.176
Cu(1)	0.017	P(2)*	−0.126
C. $0.8214X - 0.3237Y - 0.4697Z = 1.497$			
Cu(1)	−0.028	Cu(3)	−0.029
Cu(2)	0.028	Cu(4)	0.030
D. $-0.8261X + 0.3098Y + 0.4707Z = 0.312$			
C(37)	0.221	C(54)	0.001
C(38)	−0.104	C(61)	0.169
C(45)	0.072	C(62)	−0.242
C(46)	−0.182	Ir(1)*	0.300
C(53)	0.064		
E. $0.8291X - 0.3132Y - 0.4632Z = 3.363$			
C(69)	0.057	C(86)	−0.191
C(70)	−0.139	C(93)	0.138
C(77)	0.127	C(94)	−0.060
C(78)	−0.060	Ir(2)*	0.273
C(85)	0.126		

[a] Least-squares planes are defined in terms of the cartesian coordinates X, Y, Z. These are related to the fractional cell coordinates by the transformation $[X, Y, Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [b] Atoms marked with an asterisk were given zero weight in calculating the least-squares planes. All other atoms were given unit weight.

Table V. Selected Torsional Angles (deg)

Ir(1)-C(37)-C(38)-C(39)	161.1	Ir(2)-C(69)-C(70)-C(71)	171.8
Ir(1)-C(45)-C(46)-C(47)	121.2	Ir(2)-C(77)-C(78)-C(79)	110.0
Ir(1)-C(53)-C(54)-C(55)	114.4	Ir(2)-C(85)-C(86)-C(87)	130.7
Ir(1)-C(61)-C(62)-C(63)	167.7	Ir(2)-C(93)-C(94)-C(95)	129.7

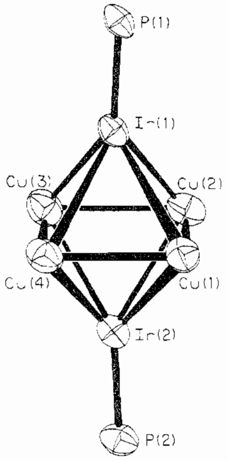

Figure 1. Thermal ellipsoids for the $Cu_4Ir_2P_2$ "core" of the $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ molecule.

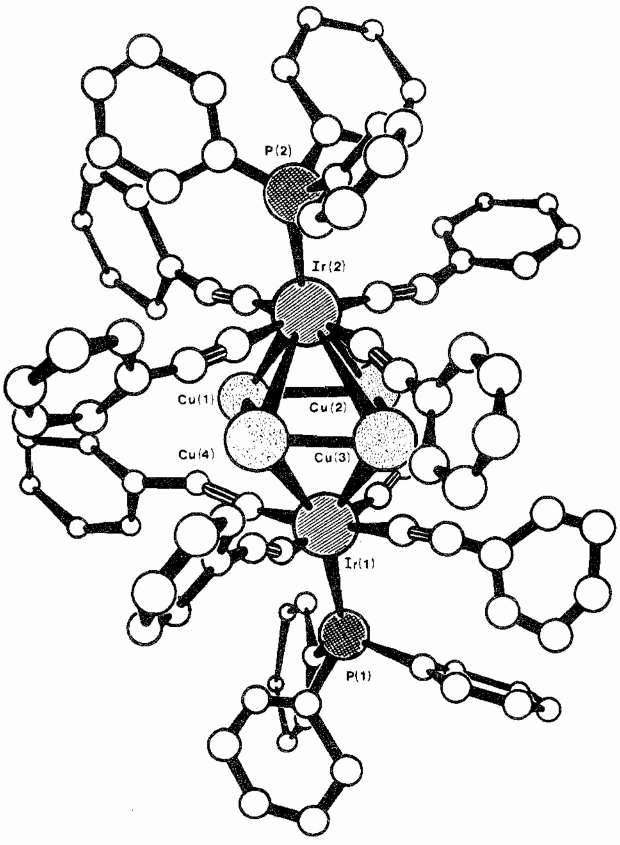

Figure 2. Molecular configuration for $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$.

compounds of iridium in lower formal oxidation states (see Table VI). This shortening may be due to a lack of competition for back-donated (d_π-d_π) electron density from iridium to phosphorus in the cluster complex; it could also be a function of overall iridium d-orbital contraction due to extra *net* positive charge on the iridium atoms in the cluster relative to the charge on the iridium atoms in the examples listed in Table VI: clearly, no unique explanation is possible.

The eight iridium-carbon σ bonds range from 1.982 (26) to 2.109 (21) Å, the average being 2.044 ± 0.039 Å. This value is consistent with the "calculated value" of ~2.05-2.08 Å based on the covalent radii of sp-hybridized carbon (0.69 Å)[46] and octahedral iridium(III) (~1.36-1.39 Å).[47,48]

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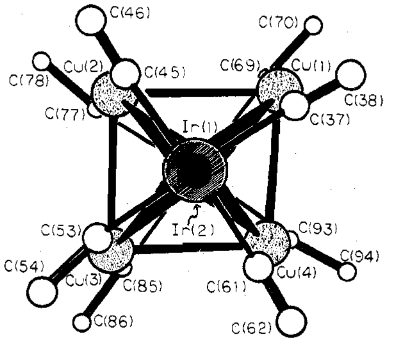


Figure 3. Numbering of atoms in the central $Cu_4Ir_2P_2(C{\equiv}C)_8$ portion of the molecule. Note the approximate D_4 symmetry of the cluster and surrounding ligands.

Table VI. Selected Ir-P Bond Distances

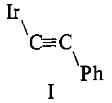
Complex	Dist, A	Ref
$[Ir(O_2)(diphos)_2][PF_6]$	2.452 (9) 2.349 (7) 2.336 (7) 2.283 (7)	22
$IrCl(CN)(NCS)(CO)(PPh_3)_2$	2.418 (3)	23
$[IrCl(CO)(NO)(PPh_3)_2][BF_4]$	2.408 (3) 2.407 (3)	24
$IrBr(CO)(TCNE)(PPh_3)_2$	2.402 (3) 2.397 (3)	25
$Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$	2.40 (av)	26
$Ir(O_2)I(CO)(PPh_3)_2$	2.391 (8) 2.386 (8)	27
$[Ir\{N_4(FC_6H_4)_2\}(CO)(PPh_3)_2][BF_4]$	2.383 (4) 2.340 (4)	28
$Ir(O_2)Cl(CO)(PPh_3)_2$	2.38 (1) 2.36 (1)	29
$[Ir(diphos)_2(CO)]Cl$	2.37 (2) 2.37 (2)	30
$[Ir(C_3Ph_3)Cl(CO)(PMe_3)_2][BF_4]$	2.369 (5) 2.360 (5)	31
$IrCl_2(NO)(PPh_3)_2$	2.367 (2)	32
$[IrI(CO)(NO)(PPh_3)_2][BF_4]$	2.367 (10) 2.353 (11)	33
$Ir_4(CO)_{10}(PPh_3)_2$ $Ir_4(CO)_9(PPh_3)_3$	2.36 (av)	34
$IrCl(SO_2)(CO)(PPh_3)_2$	2.359 (9) 2.328 (8)	35
$IrI(CH_3)(NO)(PPh_3)_2$	2.348 (3)	36
$[IrH(NO)(PPh_3)_3][ClO_4]$	2.346 (9) 2.341 (8) 2.334 (8)	37
$IrCl(CO)_2(PPh_3)_2$	2.341 (7) 2.322 (7)	38
$[Ir(NO)_2(PPh_3)_2][ClO_4]$	2.339 (3)	39
$Ir(CH_3)(C_8H_{12})[Ph_2P(CH_2)_3PPh_2]$	2.337 (4) 2.309 (4)	40
$Ir(CH_3)(C_8H_{12})(PPhMe_2)_2$	2.329 (5) 2.316 (5)	41
$Ir(NO)(CO)(PPh_3)_2$	2.324 (2) 2.323 (2)	42
$IrH(CO)(NCCH{=}CHCN)(PPh_3)_2$	2.317 (3)	43
$Ir(SnCl_3)(C_7H_8)(PPhMe_2)_2$	2.309 (2) 2.306 (2)	44
$Ir(CH_3)(C_8H_{12})(diphos)$	2.308 (3)	45
$Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$	2.268 (7) 2.248 (8)	This work

The copper-acetylene π linkages are asymmetric with Cu-C(α) distances ranging from 1.871 (26) to 2.076 (23) Å [average 1.986 ± 0.070 Å] and Cu-C(β) distances ranging from 2.142 (26) to 2.254 (28) Å [average 2.185 ± 0.042 Å].

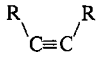
Simultaneous metal-acetylide σ bonding and acetylide-metal π bonding are rather unusual but have been reported previously in $[PhC{\equiv}CCu]_n$,[49] $[PhC{\equiv}CCuPMe_3]_4$,[50] and $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CPh)CuCl]_2$.[51] However, in each of these three species, the copper-acetylide π interaction is essentially symmetrical: in $[PhC{\equiv}CCu]_n$, Cu-C(α) = 2.13 Å (average) as compared with Cu-C(β) = 2.15 Å (average); in $[PhC{\equiv}CCuPMe_3]_4$, Cu-C(α) = 2.09 Å and Cu-C(β) = 2.06 Å; the corresponding distances in $[(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(C{\equiv}CPh)CuCl]_2$ are equal within experimental error, with a value of 1.99 (2) Å.

Within the $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ cluster, the C(α)-C(β) bond distances range from 1.181 (39) to 1.289 (35) Å, the average being 1.226 ± 0.037 Å. This distance is indistinguishable from that found in uncoordinated acetylenes [1.202 ± 0.005 Å][52] and may be compared to values of 1.33 and 1.24 Å in $[PhC{\equiv}CCu]_n$, 1.22 (2) and 1.24 (2) Å in $[PhC{\equiv}CCuPMe_3]_4$, and 1.27 (2) Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CPh)CuCl]_2$.

The acetylide moiety does not retain a linear configuration in the present cluster complex; Ir-C(α)-C(β) angles range from 164.0 (20) to 176.2 (20)° [average 169.9 ± 4.4°], while C(α)-C(β)-phenyl angles range from 158.4 (29) to 171.6 (28)° [average 164.7 ± 3.8°]. The Ir-C(α)-C(β)-phenyl torsional angles [see Table V] vary from 114.4 to 171.8°, with a mean value of 138.3°. It is apparent, therefore, that the Ir—C≡C—Ph systems each adopt a nonlinear configuration which is close to the transoid configuration (I). The cis-bent arrangement (II) has been observed in all structural



I



II

studies in which acetylenes are coordinated to a transition metal atom, *viz.*, $(PhC{\equiv}CPh)Pt(PPh_3)_2$ in which $d(C{\equiv}C)$ = 1.32 (9) Å and ∠(Ph—C≡C) = 140°;[53] $(PhC{\equiv}CPh)_2Nb(CO)(\pi\text{-}C_5H_5)$ in which $d(C{\equiv}C)$ = 1.35 (2) Å and ∠(Ph—C≡C) = 138 (4)°;[54] $(PhC{\equiv}CPh)Nb(CO)(\pi\text{-}C_5H_5)(\pi\text{-}C_4Ph_4)$ in which $d(C{\equiv}C)$ = 1.26 (4) Å and ∠(Ph—C≡C) = 142 (3)°;[55] $(Me_3C\text{-}C{\equiv}CMe_3)PtCl_2(p\text{-}MeC_6H_4NH_2)$ in which $d(C{\equiv}C)$ = 1.235 (18) Å and ∠(C—C≡C) = 161.6 (14) and 165.3 (14)°;[56] $(PhC{\equiv}CPh)Ni(Me_3CNC)_2$ in which $d(C{\equiv}C)$ = 1.276 (12) and

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(46) *Chem. Soc., Spec. Publ., Suppl.*, No. 18, S14s–S15s (1965). This value is obtained by deducting half of the $C(sp^3)$–$C(sp^3)$ bond distance [1.537 ± 0.005 Å] from the recognized $C(sp^3)$–$C(sp)$ distance of 1.459 ± 0.005 Å in C–C≡C systems.

(47) M. R. Churchill, *Perspect. Struct. Chem.*, 3, 91 (1970); see especially, Appendix 1 on p 157.

(48) Note that these iridium–carbon bonds are not expected to be contracted from a normal Ir–C(sp) *single*-bond distance. The possible conjugation of the iridium d_π orbitals with the acetylenic linkage will be essentially nullified by the copper–acetylene π interactions.

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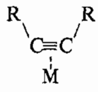
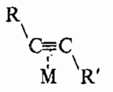
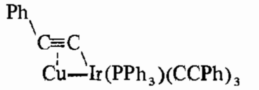
1.291 (16) Å and ∠(Ph–C≡C) = 147.5 (11), 148.2 (10), 151.3 (14), and 147.2 (14)°;[57] $(CF_3C{\equiv}CCF_3)PtCl(Me_3As)_2$ in which *d*(C≡C) = 1.32 (4) Å and ∠(CF_3–C≡C) = 135 (4) and 150 (4)°;[58] $(PhC{\equiv}CPh)_3W(CO)$ in which *d*(C≡C) = 1.30 Å and ∠(Ph–C≡C) = 139.6°;[59] and $[(NC)C{\equiv}C(CN)]Ir(CO)[C(CN){=}CH(CN)](PPh_3)_2$ in which *d*(C≡C) = 1.29 (2) Å and ∠(C–C≡C) = 139 (1) and 140 (1)°.[60] A similar cis-bent geometry is also observed in cases in which an acetylenic residue interacts with two transition metals [*e.g.*, in $(PhC{\equiv}CPh)Co_2(CO)_6$,[61] $(C_6F_6)Co_2(CO)_6$,[62] and $(PhC{\equiv}CPh)Ni_2(\pi\text{-}C_5H_5)_2$[63]], with three transition metal atoms [as in violet $(PhC{\equiv}CPh)_2Fe_3(CO)_8$[64] and $(PhC{\equiv}CPh)Fe_3(CO)_9$[65]] and with four transition metal atoms [as in $(EtC{\equiv}CEt)Co_4(CO)_{10}$[66]].

Mason[67] has interpreted the bent geometry of coordinated acetylene in terms of the promotion of the ligand from the ground state to an excited electronic state. Ingold and King[68] found the geometry of the uncoordinated ligand in its first excited state to be bent, with the trans-bent structure stabilized slightly with respect to this cis-bent structure through minimization of nonbonded repulsion interactions. Coordinated acetylenes might therefore adopt the observed cis-bent geometry in order to minimize the nonbonded repulsions between the R groups and the metal (*cf.* III and IV). By analogy, each of the acetylene fragments in the present cluster complex may be formally written as $Ph{-}C{\equiv}C{-}[Ir(PPh_3)(CCPh)_3]$. The acetylene-copper bonding may now be drawn as in V. In this case, a trans-bent conformation of the acetylene moiety is actually necessary to ensure simultaneous Cu-acetylene π bonding and a *bonding* Cu-Ir interaction.


III


IV


V

Finally we may note that the $Cu_4Ir_2P_2(C{\equiv}C)_8$ portion of the molecule has approximate, but not exact, D_4 symmetry (see Figure 3).

Bonding within the Ir_2Cu_4 Core

Ignoring the metal-metal interactions *pro tempore* and counting only the electrons associated with the valence shell of each metal atom, we find that each PPh_3 and each $PhC{\equiv}C^-$ ligand contributes two electrons to a d^5 Ir(IV) atom,[18] yielding a total of 15 valence electrons per iridium atom. Similarly, donation of four π electrons from the two adjacent acetylene linkages leads to the $d^{10}s^1$ Cu(0) atoms' each attaining a 15-electron configuration. However, each metal atom may be forced to satisfy the EAN rule by postulating a bond order of 3/4 for the 12 metal-metal interactions defining the edges of the octahedron. [A similar conclusion is reached by noting that the cluster *as a whole* has 90 outer valence electrons. Since only 84 electrons are required to fill the bonding and nonbonding orbitals in an octahedral cluster complex,[69] it follows that the outermost six electrons (*i.e.*, three electron pairs) are in antibonding orbitals. Since 12 pairs of electrons are in orbitals which are bonding *relative to metal-metal interactions* and three pairs of electrons are in orbitals which are antibonding relative to metal-metal interactions, it follows that the bond order for each of the metal-metal bonds, given by 1/12 [number of bonding pairs – number of antibonding pairs], is 3/4, as predicted by the previous empirical argument.]

Examination of the experimentally determined metal-metal distances within the $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ cluster lends considerable credence to this proposition. Thus the average copper-copper distance of 2.739 Å is slightly shorter than the average value of 2.83 Å found in $[Cu_8\{S_2CC(CN)_2\}_6{}^{4-}]$ where a Cu-Cu bond order of 2/3 is postulated[70] and is longer than the average value of 2.599 Å found in $H_6Cu_6(PPh_3)_6$, for which a bond order of 1 is claimed.[4] While copper-copper distances in polynuclear complexes are not fully understood,[71] the above trio of complexes appears to provide a self-consistent set.

While no other copper-iridium distances have been reported, the present observed value of 2.870 Å (average) seems also to be longer than a single bond. [Based upon Cu-Cu = 2.599 Å in $H_6Cu_6(PPh_3)_6$[4] and Ir-Ir = 2.73 Å in $(Ph_3P)_2Ir_4(CO)_{10}$ and $(Ph_3P)_3Ir_4(CO)_9$,[34] the predicted length of a Cu-Ir linkage of unit bond order is ~2.67.][72,73]

It should be noted that individual metal-metal distances do vary appreciably from the average values. A careful consideration of the individual distances does not indicate any clear separation into "long" and "short" bonds. Thus no direct information on the location of the antibonding orbitals is forthcoming from this study.

Acknowledgments. We thank Dr. M. I. Bruce for providing the material studied. This work was generously supported by the National Science Foundation through Grant No. GP-33018 (to M. R. C.).

Registry No. $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$, 37239-85-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the

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Contribution from the Department of Chemistry,
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Molecules with an M_4X_4 Core. II.[1]
X-Ray Crystallographic Determination of the Molecular Structure of Tetrameric Triphenylphosphinecopper(I) Bromide in Crystalline $[PPh_3CuBr]_4 \cdot 2CHCl_3$

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Received December 18, 1973 AIC309030

Tetrameric triphenylphosphinecopper(I) bromide crystallizes from chloroform as the solvated species $[PPh_3CuBr]_4 \cdot xCHCl_3$ (x = 2.0 for the idealized structure and ~1.5 for the actual crystal examined). The crystals belong to the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15], unit cell parameters being a = 28.461 (9) Å, b = 15.983 (4) Å, c = 18.044 (5) Å, and β = 112.59 (1)°. The observed density of 1.56 (2) g cm^{-3} is consistent with the value of 1.58 g cm^{-3} calculated from V = 7578 Å^3, mol wt 1802, and Z = 4. X-Ray diffraction data complete to 2θ = 40° (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved *via* a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for all nonhydrogen atoms, and with hydrogen atoms included in calculated positions, the final discrepancy indices are R_F = 6.44% and R_{wF} = 7.19% for the 2412 independent reflections. The molecule has precise (*i.e.*, crystallographically dictated) C_i symmetry with the Cu_4Br_4 core defining a "step-like" configuration—in sharp constrast to the "cubane" configuration of the Cu_4Cl_4 core in $[PPh_3CuCl]_4$. Two copper atoms, Cu(1) and Cu(1′), have a tetrahedral coordination geometry, while the other two (Cu(2) and Cu(2′)) are in trigonal-planar coordination sites. Copper-bromine distances range from 2.377 (2) to 2.664 (2) Å, while intramolecular copper· · ·copper distances are Cu(1)· · ·Cu(2′) = 2.991 (2), Cu(1′)· · ·Cu(2) = 2.991 (2), and Cu(1)· · ·Cu(1′) = 3.448 (3) Å.

Introduction

Our recent involvement with the polynuclear hydridocopper complex $(PPh_3CuH)_6$,[2,3] in which the copper-copper distances ranged from 2.494 (6) to 2.674 (5) Å, has led us to investigate a number of tetrameric phosphine (and arsine) copper(I) halides. Prior to this series of studies, only one structural investigation of such a species had been reported, Wells (in 1936) having found a copper· · ·copper distance of 2.60 Å in $(AsEt_3CuI)_4$.[4,5] Since Mason and Mingos[6] have demonstrated that the intermetallic bond order is greater (*i.e.*, the metal· · ·metal distance should be shorter) in hydrido-bridged *vis a vis* the analogous halogeno-bridged species, it seems clear that our investigations are warranted.

Following a single-crystal X-ray diffraction study of $(PPh_3CuCl)_4$ (in which Cu· · ·Cu distances were found to range from 3.118 (1) to 3.430 (1) Å),[1] we embarked on an analysis of the bromo analog, $(PPh_3CuBr)_4$. We expected to be able to follow variations in copper· · ·copper distance within cubane-like $(PPh_3CuX)_4$ species as a function of X; instead, serendipitously, we found that the Cu_4Br_4 core in $(Ph_3PCuBr)_4$ *did not* define a cube but, rather, formed a new framework, which we term a "step" structure. Preliminary results of this study have appeared previously;[7] a full account appears below.

Experimental Section

Collection and Reduction of the X-Ray Diffraction Data. The complex was prepared *via* the procedure of Jardine, Rule, and Vohra.[8] Crystals were obtained by the slow evaporation of a saturated solution of $(PPh_3CuBr)_4$ in chloroform. The crystals are initially white but become yellow following prolonged exposure to X-irradiation; significant decomposition of the crystals occurs in an X-ray beam (*vide infra*).

The crystal chosen for the single-crystal X-ray diffraction study was a regular parallelepiped bounded by well-formed {011} and {100} faces. Dimensions were $(100) \rightarrow (\bar{1}00)$ = 0.6 mm, $(011) \rightarrow (0\bar{1}\bar{1})$ = 0.3 mm, and $(0\bar{1}1) \rightarrow (01\bar{1})$ = 0.3 mm.

A preliminary photographic study, using $h(0-3)l$ and $hk(0-3)$ precession photographs along with b and c cone-axis photographs, revealed C_{2h} $(2/m)$ Laue symmetry for the diffraction pattern, provided approximate unit-cell parameters, and showed the following systematic absences: hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. These extinctions are consistent either with the noncentrosymmetric monoclinic space group Cc (C_s^4; No. 9)[9] or with the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15).[9] The successful solution of the structure proves the latter, centrosymmetric, case to be the true space group.

The crystal was aligned and centered on a Picker FACS-1 diffractometer with a^* coincident with the instrumental ϕ axis. Under "high-resolution" conditions,[10] the 2θ, ω, and χ settings were determined for the resolved Mo Kα_1 peaks (λ 0.70930 Å[11]) of 12 high-angle ($2\theta \approx 40°$) reflections which were well-dispersed in reciprocal space. These values were used in a least-squares refinement of the cell and orientation parameters. The resulting unit cell parameters (at 25 ± 1°) are a = 28.4606 (87) Å, b = 15.9831 (37) Å, c =

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