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Synthesis and Structure of a Triiridium Cluster with a Tridentate (η^1-P_1,μ-P_2,η^2-C=C) Ligand

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The reaction of $Ir(CO)_2$(*p*-toluidine)Cl with *trans*-bis(1,2-diphenylphosphino)ethylene in the presence of CO and Zn yielded $Ir_3(CO)_7$(μ-(*cis*-PPhCH=CHPPh$_2$)). The complex formed orange-red multifaceted crystals; the structure was determined at −35 °C and found to be characterized by the monoclinic space group $P2_1/c$ with unit cell constants a = 12.574 (5) Å, b = 10.917 (3) Å, c = 21.606 (5) Å, β = 104.84 (3)° and Z = 4. Full-matrix least-squares refinement converged to R = 0.038 and R_w = 0.041. The average Ir–Ir bond distance in the triangular cluster is 2.771 (1) Å. The *cis*-PPhCH=CHPPh$_2$ fragment acts as a tridentate (η^1-P_1,μ-P_2,η^2-C=C) ligand.

Introduction

The literature of triangular trinuclear iridium clusters is sparse. The only known examples are the cationic clusters $[(IrLL'H_2)_3(\mu_3\text{-}H)][PF_6]_2$, where L = PCy_3 or P-*i*-Pr_3 and L′ = pyridine,[2a] and $[Ir_3H_7(dppp)_3](BF_4)_2$.[2b] The crystal structure of the former complex (with L = PCy_3 and L′ = pyridine) has been described.[2a]

Using *trans*-bis(1,2-diphenylphosphino)ethylene in an attempt to prepare oligomer tetranuclear clusters bridged with diphosphine,[3] we instead isolated a novel trinuclear iridium cluster containing the cis ligand which had undergone phosphorus–carbon bond cleavage. Other phosphide-bridged compounds have been obtained by cleavage of tertiary phosphines in solvolytic reactions of transition metals.[4–6]

The accumulated analytical data coupled with the phosphorus and proton NMR results, which were incompatible with the bis-phosphine ligand in its original form, led us to determine the molecular structure by X-ray methods.

Experimental Section

In a typical experiment, $Ir(CO)_2$(*p*-toluidine)Cl (200 mg), *trans*-bis(1,2-diphenylphosphino)ethylene (100 mg), (Strem typical purity 95%, with the cis isomer being the major impurity; ^{31}P NMR showed one peak at 8.7 ppm to higher field of external H_3PO_4), and acid-washed mossy zinc (3.8 g) were added to an oxygen-free solution of THF (28 mL) and H_2O (1.2 mL) in a Parr pressure bottle.[7] The system was charged with 4 atm of CO and heated at 90 °C for 45 min. After cooling, the bottle was depressurized and the reaction mixture filtered. Following removal of the solvent, the residue was fractionated on a silica gel column with a mixture of hexane and methylene chloride (about 6:1) as elutant. Two major bands developed on the column: a yellow-orange band (the title compound) and a slower moving violet band.[8] Orange crystals of the title compound (15 mg) were grown from a methylene chloride/hexane solution. Infrared (CH_2Cl_2): ν(C–O) 2071, 2029, 2016, 1991, 1956 cm^{-1}. 220-MHz ^{1}H NMR ($CDCl_3$): δ 3.03 (d of d of d, 1 H, J_{P_1H} = 14.4 Hz, J_{P_2H} = 37 Hz, J_{HH} = 4.7 Hz) 3.73 (d of d of d, 1 H, J_{P_1H} = 33.1 Hz, J_{P_2H} = 9.7 Hz, J_{HH} = 4.7 Hz) 6.9–7.7 (m, 15 H). 36.4-MHz $^{31}P\{^1H\}$ NMR ($CDCl_3$): 99.44 (d, 1 P, J_{PP} = 37.8 Hz), −22.86 (d, 1 P J_{PP} = 37.8 Hz) ppm (relative to external H_3PO_4). Anal. Calcd for $C_{27}H_{17}Ir_3O_7P_2$: C, 29.47; H, 1.55; Ir, 52.35; P, 6.44. Found: C, 29.82; H, 1.55; Ir, 54.11; P, 7.30. Molecular weight: calcd, 1100.3; found, 1091. The elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, New York, NY.

Table I. Experimental Summary for $Ir_3(CO)_7(PhPC_2H_2PPh_2)$

Crystal Data at −35 °C[a]

a, Å	12.574 (5)	F(000), electrons	1984
b, Å	10.917 (3)	systematic absences	hkl, no conditions;
c, Å	21.606 (5)		$h0l$, $l = 2n + 1$;
β, deg	104.84 (3)		$0k0$, $k = 2n + 1$
V, Å^3	2867 (3)	cryst system	monoclinic
d_{calcd}, g cm^{-3}	2.54	space group	$P2_1/c$ (No. 14)
		fw	1091.8
		empirical formula	$C_{27}H_{17}Ir_3O_7P_2$

Data Collection at −35 °C[b]

radiation (Mo Kα), Å	0.71069
mode	ω scan
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ maximum
scan rate, deg min^{-1}	variable
check reflctns	4 measd after every 96 reflctns
2θ range, deg	4.0–52.5
total independent reflctns measd	5477
data cryst faces	(001), (00$\bar{1}$), (011), (0$\bar{1}\bar{1}$), (0$\bar{1}$1), (01$\bar{1}$), (10$\bar{2}$), ($\bar{1}$02), (101), (102)
abs coeff [μ(Mo Kα), cm^{-1}]	148.5
range of transmission factors	0.160–0.113
p factor	0.02

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with 22° < 2θ < 24°.
[b] Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator and Syntex LT-1 inert-gas low-temperature delivery system.

Structure Solution and Refinement

Air-stable multifaceted orange-red crystals of the title compound were grown by the slow evaporation of a methylene chloride/hexane solution. A suitable single crystal was mounted on a glass fiber and transferred to a Syntex P2$_1$ diffractometer, where it was maintained in a cold (−35 °C) stream of dry nitrogen for the duration of the

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(1) (a) University of Delaware. (b) The University of Texas at Austin.

(2) (a) D. F. Chodosh, R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Organomet. Chem.*, **161**, C67 (1978). (b) H. H. Wang and L. H. Pignolet, *Inorg. Chem.*, **19**, 1470 (1980).

(3) Two tetranuclear iridium clusters linked by diphosphines have been synthesized. (a) $[Ir_4(CO)_{11}]_2$(+)DIOP: J. Lieto, J. J. Rafalko, J. V. Minkiewicz, P. W. Rafalko, and B. C. Gates In "Fundamental Research in Homogeneous Catalysis", Vol. 3, M. Tsutsui, Ed., Plenum Press, New York, 1979. (b) $[Ir_4(CO)_{11}]_2PPh_2(CH_2)_6PPh_2$: J. J. Rafalko and B. C. Gates, unpublished results.

(4) (a) J. R. Blickensderfer and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 2681 (1975). (b) R. Mason, I. Sotofte, S. D. Robinson, and M. F. Uttley, *J. Organomet. Chem.*, **46**, C61 (1972).

(5) P. L. Bellen, C. Benedicenti, G. Caglio, and M. Manasew, *J. Chem. Soc., Chem. Commun.*, 946 (1973).

(6) C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Chem. Commun.*, 87 (1972).

(7) U. Klabunde, *Inorg. Synth.*, **15**, 82 (1974).

(8) The infrared spectrum of this product in methylene chloride exhibited four bands in the CO stretching region: 2082, 2038, 1982 and 1827 cm^{-1}. The yield of this complex increased relative to that of the title compound as the reactant ratio of $Ir(CO)_2$(*p*-toluidine)Cl to *trans*-bis(1,2-diphenylphosphino)ethylene was increased. When exposed to air overnight, the violet compound in solution decomposed.

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Table II. Fractional Coordinates and Anisotropic Thermal Parameters (×10³) for Nongroup Atoms of $Ir_3(CO)_7(PhPC_2H_2PPh_2)$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir(1)[b]	0.31099 (4)	0.10803 (4)	0.04561 (2)	268 (2)	278 (2)	288 (2)	−17 (2)	122 (2)	−7 (2)
Ir(2)[b]	0.29899 (4)	0.05412 (4)	0.16749 (2)	247 (2)	381 (3)	246 (2)	−26 (2)	85 (2)	−49 (2)
Ir(3)[b]	0.28401 (4)	0.29715 (4)	0.12668 (2)	255 (2)	307 (2)	468 (3)	−49 (2)	133 (2)	−131 (2)
P(1)	0.2451 (2)	−0.1129 (3)	0.1025 (1)	30 (1)	31 (2)	22 (1)	−1 (1)	8 (1)	2 (1)
P(2)	0.1467 (2)	0.1502 (3)	0.1057 (1)	24 (1)	34 (2)	33 (2)	−3 (1)	11 (1)	−5 (1)
O(1A)	0.2815 (8)	0.1939 (10)	−0.0911 (4)	68 (7)	75 (7)	44 (5)	−6 (6)	13 (5)	19 (5)
O(1B)	0.5536 (7)	0.0558 (9)	0.0756 (4)	31 (5)	87 (7)	47 (5)	8 (5)	17 (4)	8 (5)
O(2A)	0.5463 (8)	0.0084 (11)	0.2180 (5)	38 (6)	120 (10)	54 (6)	21 (6)	2 (5)	10 (6)
O(2B)	0.2308 (9)	0.0392 (11)	0.2929 (5)	71 (7)	112 (9)	48 (6)	−21 (7)	35 (5)	−11 (6)
O(3A)	0.5348 (8)	0.3145 (9)	0.1702 (5)	36 (5)	67 (7)	90 (8)	−7 (5)	12 (5)	−17 (6)
O(3B)	0.2384 (9)	0.4730 (11)	0.0135 (6)	64 (7)	72 (8)	101 (9)	−15 (6)	−6 (6)	28 (7)
O(3C)	0.2083 (11)	0.4309 (16)	0.2324 (8)	98 (10)	209 (18)	175 (16)	−33 (11)	82 (11)	−150 (15)
C(1A)	0.2943 (10)	0.1602 (11)	−0.0400 (6)	33 (6)	40 (7)	50 (8)	−8 (6)	18 (6)	−1 (6)
C(1B)	0.4626 (10)	0.0776 (11)	0.0637 (5)	36 (7)	42 (7)	30 (6)	1 (5)	16 (5)	6 (5)
C(2A)	0.4524 (10)	0.0244 (12)	0.1997 (5)	35 (7)	59 (8)	27 (6)	−3 (6)	1 (5)	1 (6)
C(2B)	0.2596 (11)	0.0424 (14)	0.2470 (6)	45 (8)	69 (9)	37 (7)	−9 (7)	16 (6)	−1 (7)
C(3A)	0.4415 (10)	0.3093 (12)	0.1540 (6)	31 (7)	48 (8)	58 (8)	−2 (6)	14 (6)	−16 (6)
C(3B)	0.2542 (11)	0.4069 (13)	0.0571 (8)	39 (8)	46 (9)	89 (12)	3 (7)	18 (8)	10 (8)
C(3C)	0.2369 (13)	0.3798 (16)	0.1947 (10)	51 (9)	57 (11)	96 (17)	−26 (9)	26 (11)	−47 (12)
C(A)	0.1888 (9)	−0.0373 (10)	0.0281 (5)	27 (6)	30 (6)	25 (5)	−8 (5)	7 (4)	5 (4)
C(B)	0.1345 (9)	0.0777 (10)	0.0301 (5)	30 (6)	29 (6)	36 (6)	−3 (5)	11 (5)	−10 (5)
H(CA)[c]	0.178 (8)	−0.085 (9)	−0.003 (5)						
H(CB)[c]	0.088 (8)	0.108 (9)	−0.007 (5)						

[a] See Figure 1 for identities of the atoms. Numbers in parentheses in this and succeeding tables are the estimated standard deviations in the units of the least significant digits. The U_{ij} are mean-square amplitudes of vibration in Å² from the general temperature expression $\exp[-2\pi^2\cdot(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For the Ir atoms the anisotropic temperature parameters are given ×10⁴. [c] The olefinic hydrogen atoms were treated with fixed isotropic $B = 2.0$ Å².

Table III. Group Atom Fractional Coordinates and Isotropic Thermal Parameters for $Ir_3(CO)_7(PhPC_2H_2PPh_2)$

atom	x	y	z	B, Å²
Ph(1)				
C(1)	0.1397 (6)	−0.2157 (7)	0.1177 (4)	2.7 (2)
C(2)	0.0851 (7)	−0.2915 (8)	0.0679 (3)	3.5 (2)
C(3)	0.0009 (7)	−0.3677 (7)	0.0758 (4)	4.7 (3)
C(4)	−0.0288 (7)	−0.3682 (8)	0.1336 (4)	4.9 (3)
C(5)	0.0258 (7)	−0.2924 (9)	0.1835 (3)	5.0 (3)
C(6)	0.1101 (7)	−0.2162 (7)	0.1756 (3)	4.1 (3)
Ph(2)				
C(1)	0.3486 (6)	−0.2210 (6)	0.0897 (3)	2.1 (2)
C(2)	0.4062 (7)	−0.2889 (7)	0.1421 (3)	3.8 (3)
C(3)	0.4858 (7)	−0.3726 (7)	0.1351 (3)	4.4 (3)
C(4)	0.5077 (6)	−0.3885 (7)	0.0757 (4)	4.3 (3)
C(5)	0.4501 (7)	−0.3206 (8)	0.0232 (3)	3.6 (3)
C(6)	0.3705 (6)	−0.2369 (7)	0.0302 (3)	3.1 (2)
Ph(3)				
C(1)	0.0135 (5)	0.1708 (7)	0.0005 (4)	2.6 (2)
C(2)	−0.0352 (7)	0.2861 (6)	0.1181 (4)	4.0 (3)
C(3)	−0.1396 (7)	0.3002 (6)	0.1280 (4)	5.0 (3)
C(4)	−0.1954 (5)	0.1990 (8)	0.1431 (4)	4.1 (3)
C(5)	−0.1468 (6)	0.0836 (7)	0.1483 (4)	4.1 (3)
C(6)	−0.0423 (6)	0.0695 (6)	0.1384 (4)	3.2 (2)

diffraction experiments. A summary of the pertinent crystal data and details of the X-ray diffraction data collection are presented in Table I. An analysis[9] of the check reflection data indicated only random fluctuations in intensity, with all computed correction factors being less than 0.3σ. Therefore, no decay correction was applied to the data. Preliminary processing of the diffraction data was accomplished as described in detail previously,[10] including a correction for absorption based on measured crystal shape.

Of the 5477 measured reflections, 4535 with $I_0/\sigma(I_0) > 2.5$ were used in the structure solution and refinement. Initial positions of the three iridium atoms were determined from a sharpened Patterson map. The remainder of the nonhydrogen atoms were then located from successive electron density and difference density maps. There was, however, some difficulty because of the presence of series termination ripples near the cluster of metal atoms. The structure was then refined by standard full-matrix least-squares methods,[11] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$. Neutral-atom scattering factors for Ir, P, O, C,[12] and H[13] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[12] for anomalous dispersion were applied to the Ir and P scattering curves. Throughout the refinement, the phenyl rings were treated as rigid groups of D_{6h} symmetry, with C–C = 1.392 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. Phenyl ring carbon atoms were refined isotropically, while the hydrogens of these rings were assigned a fixed isotropic thermal parameter of 4.1 Å². After convergence of this model to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.082$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.084$, a difference electron density map allowed location of the two olefinic hydrogen atoms. Further refinement, treating the olefin hydrogens isotropically with fixed $B = 2.0$ Å², all other nongroup atoms anisotropically, and the phenyl rings as described earlier, resulted in convergence at $R = 0.038$ and $R_w = 0.041$. In the final cycle of refinement, the shift/esd ratios were less than 0.02 for all nongroup positional parameters, less than 0.14 for nongroup thermal parameters, and less than 0.12 for group parameters. A final difference electron density map revealed the largest remaining peak to be 0.8 e Å^{-3}.

Fractional crystallographic coordinates for nongroup atoms, along with their thermal parameters, are presented in Table II. Group atom fractional coordinates and isotropic thermal parameters are provided in Table III and the rigid group parameters in Table IV. Bond lengths and bond angles, with their corresponding standard deviations, are given in Tables V and VI, respectively. A tabulation of final observed and calculated structure factor amplitudes is available.[14]

Results and Discussion

The reaction of $Ir(CO)_2$(*p*-toluidine)Cl with *trans*-bis(1,2-diphenylphosphino)ethylene in the presence of CO and Zn yielded an iridium cluster complex. The olefinic proton–proton coupling constant of 4.7 Hz clearly indicated a cis rather than trans disposition of hydrogen atoms at the double bound. The

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[9] W. H. Henslee and R. E. Davis, *Acta Crystallogr., Sect. B*, **B31**, 1511 (1975).

[10] P. E. Riley and R. E. Davis, *Acta Crystallogr., Sect. B*, **B32**, 381 (1976).

[11] A listing of principal computer programs used in this work is given in ref 10.

[12] "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

[13] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[14] Supplementary material.

Table IV. Group Parameters for $Ir_3(CO)_7(PhPC_2H_2PPh_2)$[a]

group	x_0	y_0	z_0	ϕ	θ	ρ
Ph(1)	0.1397 (6)	−0.2157 (7)	0.1177 (4)	−0.888 (6)	2.818 (4)	−1.384 (6)
Ph(2)	0.3486 (6)	−0.2210 (6)	0.0897 (3)	0.814 (5)	−2.844 (4)	1.618 (5)
Ph(3)	0.0135 (5)	0.1708 (7)	0.1233 (4)	−1.692 (5)	2.735 (5)	−2.932 (5)

[a] For a description of these group parameters see R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). Angular coordinates are in radians. The internal coordinate system of the phenyl ring has been defined elsewhere: P. E. Riley and R. E. Davis, *Acta Crystallogr., Sect. B*, B31, 2928 (1975).

Table V. Bond Lengths (Å) for $Ir_3(CO)_7(PhPC_2H_2PPh_2)$

Ir(1)-Ir(2)	2.740 (1)	Ir(2)-P(2)	2.289 (3)	P(1)-C(1) (Ph1)	1.830 (8)	C(1B)-O(1B)	1.133 (15)
Ir(1)-Ir(3)	2.785 (1)	Ir(2)-C(2A)	1.904 (12)	P(1)-C(1) (Ph2)	1.829 (7)	C(2A)-O(2A)	1.158 (16)
Ir(1)-C(A)	2.174 (11)	Ir(2)-C(2B)	1.912 (13)	P(2)-C(B)	1.788 (12)	C(2B)-O(2B)	1.140 (16)
Ir(1)-C(B)	2.183 (11)	Ir(3)-P(2)	2.316 (3)	P(2)-C(1) (Ph3)	1.825 (7)	C(3A)-O(3A)	1.137 (16)
Ir(1)-C(1A)	1.896 (13)	Ir(3)-C(3A)	1.921 (13)	C(A)-C(B)	1.435 (16)	C(3B)-O(3B)	1.163 (21)
Ir(1)-C(1B)	1.875 (12)	Ir(3)-C(3B)	1.884 (16)	C(A)-H(CA)	0.84 (10)	C(3C)-O(3C)	1.121 (25)
Ir(2)-Ir(3)	2.787 (1)	Ir(3)-C(3C)	1.942 (19)	C(B)-H(CB)	0.93 (11)		
Ir(2)-P(1)	2.296 (3)	P(1)-C(A)	1.784 (11)	C(1A)-O(1A)	1.136 (17)		

Table VI. Bond Angles (Deg) for $Ir_3(CO)_7(PhPC_2H_2PPh_2)$

Ir(1)-Ir(2)-Ir(3)	60.5 (0)	P(1)-C(A)-Ir(1)	94.7 (5)
Ir(2)-Ir(3)-Ir(1)	58.9 (0)	P(2)-C(B)-C(A)	118.9 (8)
Ir(3)-Ir(1)-Ir(2)	60.6 (0)	P(2)-C(B)-Ir(1)	86.9 (5)
C(1A)-Ir(1)-C(1B)	96.3 (5)	P(2)-C(B)-H(CB)	122 (6)
C(1A)-Ir(1)-Ir(2)	169.5 (4)	H(CB)-C(B)-C(A)	119 (6)
C(1A)-Ir(1)-Ir(3)	113.0 (4)	H(CB)-C(B)-Ir(1)	118 (6)
C(1A)-Ir(1)-C(A)	98.8 (5)	C(1) (Ph3)-P(2)-C(B)	112.2 (5)
C(1A)-Ir(1)-C(B)	92.4 (5)	C(1) (Ph3)-P(2)-Ir(2)	127.6 (3)
C(1B)-Ir(1)-Ir(2)	93.7 (3)	C(1) (Ph3)-P(2)-Ir(3)	123.5 (3)
C(1B)-Ir(1)-Ir(3)	106.3 (3)	Ir(2)-P(2)-Ir(3)	74.5 (1)
C(1B)-Ir(1)-C(A)	122.9 (5)	P(1)-Ir(2)-Ir(1)	70.3 (1)
C(1B)-Ir(1)-C(B)	160.8 (5)	P(1)-Ir(2)-Ir(3)	125.3 (1)
C(A)-Ir(1)-Ir(2)	78.4 (3)	P(2)-Ir(2)-Ir(1)	65.5 (1)
C(A)-Ir(1)-Ir(3)	117.1 (3)	P(2)-Ir(2)-Ir(3)	53.2 (1)
C(B)-Ir(1)-Ir(2)	79.1 (3)	P(2)-Ir(2)-P(1)	86.3 (1)
C(B)-Ir(1)-Ir(3)	85.8 (3)	C(3A)-Ir(3)-Ir(1)	87.8 (4)
C(B)-Ir(1)-C(A)	38.5 (4)	C(3A)-Ir(3)-Ir(2)	89.3 (4)
C(2A)-Ir(2)-Ir(1)	95.0 (3)	C(3A)-Ir(3)-C(3B)	100.4 (6)
C(2A)-Ir(2)-Ir(3)	104.9 (4)	C(3A)-Ir(3)-C(3C)	103.0 (6)
C(2A)-Ir(2)-C(2B)	97.6 (5)	C(3A)-Ir(3)-P(2)	140.0 (4)
C(2A)-Ir(2)-P(1)	101.6 (4)	C(3B)-Ir(3)-Ir(1)	90.0 (5)
C(2A)-Ir(2)-P(2)	155.4 (4)	C(3B)-Ir(3)-Ir(2)	147.3 (5)
C(2B)-Ir(2)-P(1)	113.2 (4)	C(3B)-Ir(3)-C(3C)	105.8 (7)
C(2B)-Ir(2)-P(1)	100.6 (4)	C(3B)-Ir(3)-P(2)	107.4 (5)
C(2B)-Ir(2)-Ir(1)	165.8 (4)	C(3C)-Ir(3)-Ir(1)	158.6 (5)
C(2B)-Ir(2)-Ir(3)	109.6 (4)	C(3C)-Ir(3)-Ir(2)	102.2 (5)
C(1) (Ph1)-P(1)-C(1) (Ph2)	102.0 (3)	C(3C)-Ir(3)-P(2)	96.5 (5)
C(1) (Ph1)-P(1)-C(A)	107.3 (4)	P(2)-Ir(3)-Ir(1)	64.4 (1)
C(1) (Ph2)-P(1)-C(A)	107.9 (5)	P(2)-Ir(3)-Ir(2)	52.3 (1)
C(1) (Ph1)-P(1)-Ir(2)	119.4 (2)	O(1A)-C(1A)-Ir(1)	177.6 (11)
C(1) (Ph2)-P(1)-Ir(2)	119.7 (2)	O(1B)-C(1B)-Ir(1)	177.7 (11)
C(A)-P(1)-Ir(2)	99.8 (4)	O(2A)-C(2A)-Ir(2)	178.1 (11)
C(B)-C(A)-P(1)	117.5 (8)	O(2B)-C(2B)-Ir(2)	176.1 (12)
C(B)-C(A)-Ir(1)	71.1 (6)	O(3A)-C(3A)-Ir(3)	179.0 (12)
C(B)-C(A)-H(CA)	126 (7)	O(3B)-C(3B)-Ir(3)	178.0 (13)
H(CA)-C(A)-P(1)	113 (7)	O(3C)-C(3C)-Ir(3)	177.4 (18)
H(CA)-C(A)-Ir(1)	124 (7)		

chemical shifts of these hydrogens, δ 3.03 and 3.73, were upfield from the free ligand by 3.97 and 3.27 ppm, also strongly indicative of complexation to a metal center. The chemical shift separation of the phosphorus atoms, 122.3 ppm, suggested significantly different environments for the two atoms, but the fact that they were coupled (J_{PP} = 37.5 Hz) implied that they were probably chelated to the same iridium atom. Since there were no CO stretching modes below 1956 cm^{-1} in the infrared spectrum, it was at least clear that all carbonyl groups were bonded in terminal positions.

The complex was shown to be $Ir_3(CO)_7(\mu_3\text{-}(cis\text{-}PPhCH{=}CHPPh_2))$, with the structure determined by X-ray crystallography depicted in Figure 1. The Ir–Ir lengths of 2.787 (1), 2.785 (1), and 2.740 (1) Å are in the range of single bond lengths observed in other iridium clusters. The first two distances are slightly greater than those found in $Ir_4(CO)_{12}$ (2.68 Å, mean)[15] and $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ (both 2.73 Å, mean).[16] However, they are comparable to some individual metal–metal bond lengths in $Ir_4(CO)_{10}$(+)-DIOP (2.775 Å),[17] $Ir_4(CO)_8[(MeCO_2)_2C_2]_4$ (2.810 Å),[18] and

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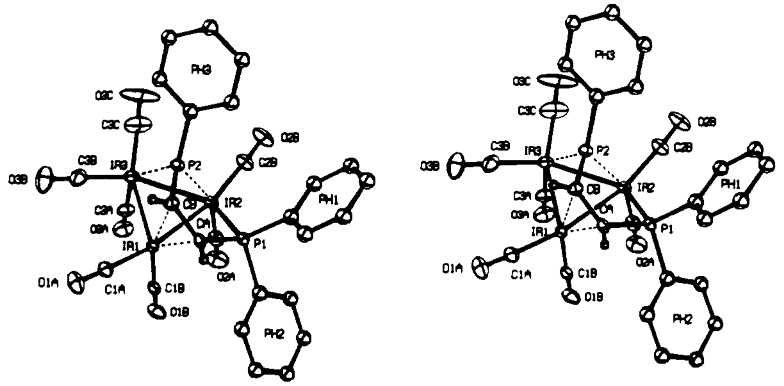

Figure 1. Stereoview of $Ir_3(CO)_7(PhPCH{=}CHPPh_2)$, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogens as spheres of radius 0.1 Å. Phenyl hydrogens are omitted for clarity.

$[H_2Ir_4(CO)_{10}]^{2-}$ (2.802 Å).[19] All of the seven carbonyls are terminal. The deviation from linearity of the Ir–C–O bonds is small, with the angles ranging from 176.1 to 179.0°.

The *cis*-$PPhCH{=}CHPPh_2$ fragment coordinates to the cluster as a tridentate ligand. P(1) coordinates to Ir(2), and P(2) bridges Ir(2) and Ir(3). The carbon–carbon double bond π bonds to Ir(1). The Ir–P bond lengths for the phosphido phosphorus, 2.289 (3) and 2.316 (3) Å, and the nonbridging phosphorus, 2.296 (3) Å, are typical of these bonding modes.[17,20] The iridium–olefinic carbon distances of 2.174 (11) and 2.183 (11) Å and the carbon–carbon distance of 1.435 (16) Å are similar to those observed for $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$.[21]

$Ir_3(CO)_7(\mu$-(*cis*-$PPCH{=}CHPPh_2))$ is the first known neutral triangular trinuclear iridium cluster. Although *cis*-bis(1,2-diphenylphosphino)ethane was not observed in NMR spectra of the *trans*-diphosphine starting material, the low yield of the cluster makes the source of the incorporated cis ligand uncertain—it was likely either an isomerization product of the trans ligand or formed from a minor impurity in the starting material. Synthesis of the cluster was unexpected, since the reaction of other tertiary phosphines (e.g., PPh_3, $P(p\text{-tol})_3$, and PEt_3) with $Ir(CO)_2(p\text{-toluidine})Cl$ under similar reaction conditions results in the formation of the tetranuclear clusters $Ir_4(CO)_{11}PR_3$ and $Ir_4(CO)_{10}(PR_3)_2$.

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Registry No. $Ir_3(CO)_7(\mu_3$-(*cis*-$PPhCH{=}CHPPh_2))$, 78149-28-7; $Ir(CO)_2(p\text{-toluidine})Cl$, 14243-22-2; *trans*-$Ph_2PCH{=}CHPPh_2$, 983-81-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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A-Frames

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The electronic structure of molecular A-frames is discussed. These are binuclear transition-metal complexes of the type $LM[\mu\text{-E}{\cdots}\text{E}]_2[\mu\text{-X}]ML$ where E···E is a bidentate ligand of the dpm or dam class and X is a bridging group such as H, Cl, S, H, CO, NO, SO_2, or acetylene. The orbitals of the invariant M_2L_6 fragment are constructed and then interacted with X. Once ambiguities in electron counting in these complexes are clarified, a consistent picture of the bonding in these molecules emerges. Among the subjects treated are metal–metal bonding in the A-frames, the possible existence of some complexes pointed to by the computed orbital patterns or isolobal analogies, and the geometrical changes at the metal centers accompanying parallel and perpendicular coordination of acetylenes.

Molecules in which two or more metal centers are held in proximity to each other, yet in which access to the metals is controlled by the ligands, offer in principle the possibility of systematic cooperative binding and activation of substrates. One such class of molecules currently under investigation comprises the so-called molecular "A-frames".[1] The A-frames are a specific set of $M_2L_6(\text{ligand})^2$ complexes with the metals held near each other by bidentate dpm or dam bridging ligands

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