Mixed-Metal Cluster Chemistry. Site-Selective Reactions of CpWIr₃(CO)₁₁ with PPh₃ and Bidentate Phosphines: X-ray Crystal Structures of CpWIr₃(μ-dppe)(μ-CO)₃(CO)₆, CpWIr₃(μ-dppm)(μ-CO)₃(CO)₆, and CpWIr₃(μ-dppa)(μ-CO)₃(CO)₆

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Reactions of CpWIr₃(CO)₁₁ (1) with equimolar amounts of phosphines afford the site-selective monophosphine cluster products CpWIr₃(μ-CO)₃(CO)₈₋ₓ(L) (L = PPh₃ (2a), x = 1; L = μ-dppe (2b), μ-dppm (2c), x = 2) in excellent yields (64–84%). Reaction of 1 with the linear diphosphine dppa, Ph₂PC≡CPPh₂, affords CpWIr₃(μ-dppa)(μ-CO)₃(CO)₆ (2d) in low yield (15%). From the ³¹P NMR spectrum and preliminary crystallographic results, PPh₃ has been assigned to a radial site in 2a. The structures of 2b, 2c, and 2d have been determined by single crystal X-ray diffraction studies; in these three cases, the bidentate phosphines are diaxially-coordinated. In 2d, the bidentate phosphine is highly strained, with an ∠PC≡C of 147.2(8)°. Crystal data: for 2b, space group = P1̄, a = 18.563(5) Å, b = 11.855(4) Å, c = 10.367(2) Å, α = 67.72(2)°, β = 73.54(2)°, γ = 77.44(2)°, Z = 2, N₀ = 10 230 "observed" reflections (I > 3σ(I)), R = 0.045; for 2c, space group = P2₁/c, a = 10.748(12) Å, b = 22.439(5) Å, c = 19.886(14) Å, β = 114.95(8)°, Z = 4, N₀ = 2710, R = 0.087; for 2d, space group = Pmnb, a = 21.608(4) Å, b = 17.843(3) Å, c = 10.134(3) Å, Z = 4, N₀ = 2740, R = 0.032.

Introduction

Research into mixed-metal clusters is stimulated by the belief that disparate metals within one molecule may induce new and interesting reactivity; the cooperative effects between adjacent metal centers could be enhanced by the presence of a polar metal–metal bond. Of interest also is the idea that sufficiently different metals should "select" for particular types of reagents. Some of the most fundamental reagents in organotransition metal chemistry are phosphines, and site-selectivity investigations of mixed-metal clusters with phosphines have been recently reported.[1] The vast majority of such studies have been concerned with mixed-metal clusters containing metals from the same group or from adjacent groups; investigations with mixed-metal clusters employing widely differing metals are comparitively rare. The pseudotetrahedral mixed tungsten—iridium cluster CpWIr₃(CO)₁₁ (1)[2] has previously been shown to be a precursor for a heterogeneous catalyst active in alkane hydrogenolysis,[2a,3a] and to react in solution with internal acetylenes to afford products involving C—C formation and C≡C rupture.[3] We herein report results of an investigation into the reactivity of 1 toward PPh₃ and bidentate phosphines and the characterization by single crystal X-ray studies of the site-selective reaction products.

Experimental Section

General Information. All reactions were performed under an atmosphere of dry nitrogen (high purity grade, CIG), although no special precautions were taken to exclude air during workup;

the reaction solvent dichloromethane was dried over CaH₂. All other solvents were reagent grade and used as received; petroleum ether refers to a fraction of boiling point range 40–70 °C. The progress of the reactions was monitored by analytical thin-layer chromatography (5554 Kieselgel 60 F₂₅₄, E. Merck), and the

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products were separated on 20- × 20-cm glass plates coated with 7749 Kieselgel 60 PF₂₅₄ (E. Merck). The reagents PPh₃, dppe (Ph₂PCH₂CH₂PPh₂), dppm (Ph₂PCH₂PPh₂), and dppa (Ph₂-PC≡CPPh₂) were purchased commercially (Aldrich, Strem) and used as received. The cluster CpWIr₃(CO)₁₁ was prepared by the published procedure.[2a,c]

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer FTIR 1725x spectrometer using CaF₂ optics. All NMR spectra were recorded on a Bruker AC300 FT spectrometer (¹H NMR at 300 MHz, ¹³C NMR at 75 MHz, and ³¹P NMR at 121 MHz). All ¹³C NMR spectra were obtained by spectral addition of blocks of 6000 acquisitions; the samples contained ca. 0.02 M Cr(acac)₃ and utilized a 0.5-s recycle delay. All NMR spectra were run in CDCl₃ (Aldrich); chemical shifts in ppm are referenced to internal residual solvent for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra.

Fast atom bombardment (FAB) mass spectra were obtained at the University of Adelaide on a VG ZAB 2HF mass spectrometer equipped with a FAB source of argon, typically at 10⁻⁶ mbar; the FAB gun voltage was 7.5 kV, the current was 1 mA, and the ion accelerating potential was 8 kV. The matrix used was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 M solutions in dichloromethane. A drop of the complex solution was added to a drop of the matrix and applied to the FAB probe tip. All FAB MS were calculated with m/z based on ¹⁸³W assignments and are reported in the following form: m/z, (assignment, relative intensity). Elemental microanalyses were performed by the Microanalysis Service Unit in the Department of Chemistry, University of Queensland. Decomposition temperatures and melting points were measured in sealed capillaries using a Gallenkamp melting point apparatus and are uncorrected.

Reaction of CpWIr₃(CO)₁₁ with PPh₃. An orange solution of CpWIr₃(CO)₁₁ (20.0 mg, 0.0176 mmol) and PPh₃ (4.6 mg, 0.018 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 24 h. The dark orange solution obtained was evaporated to dryness. The brownish-orange residue was dissolved in CH₂Cl₂ (ca. 1 mL) and chromatographed (3 CH₂Cl₂:2 petroleum ether) to afford two products, one of which was in trace amounts. The major product, R_f 0.70, was recrystallized from CH₂Cl₂/CH₃OH to afford orange crystals of CpWIr₃(μ-CO)₃(CO)₇(PPh₃), **2a** (20.2 mg, 84%, mp 158 °C dec). Analytical data for **2a**: IR (c-C₆H₁₂) 2075 (vs), 2063 (m), 2038 (vs), 2023 (vs), 2010 (vs, br), 1994 (vs), 1984 (m, sh), 1962 (m), 1926 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 7.41 (m, 15H, C₆H₅), 4.85 (s, 5H, C₅H₅); ¹³C NMR (CDCl₃) δ 133.67–128.45 (C₆H₅) 86.03 (C₅H₅); ³¹P NMR (CDCl₃) δ 9.19 (Ir–P); FAB MS 1368 ([M]⁺, 11), 1340 ([M –1CO]⁺, 6), 1312 ([M –2CO]⁺, 39), 1284 ([M – 3CO]⁺, 28), 1256 ([M – 4CO]⁺, 17), 1228 ([M – 5CO]⁺, 100), 1200 ([M – 6CO]⁺, 28), 1172 ([M – 7CO]⁺, 33), 1144 ([M – 8CO]⁺, 17), 1116 ([M – 9CO]⁺, 11), 1087 ([M – 10CO]⁺, 8). Anal. Calcd: C, 28.98; H 1.47. Found: C, 28.71; H, 1.48.

Reaction of CpWIr₃(CO)₁₁ with dppe. A light orange solution of CpWIr₃(CO)₁₁ (40.0 mg, 0.0350 mmol) and dppe (14.0 mg, 0.0350 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 2 h. The resultant dark orange solution was evaporated to dryness. The brown residue obtained was dissolved in CH₂Cl₂ (ca. 1.5 mL) and chromatographed (4 CH₂Cl₂:1 petroleum ether). Two bands were obtained, one in trace amounts. The major product, R_f 0.83, was recrystallized from CH₂Cl₂/CH₃OH to afford brown crystals of CpWIr₃(μ-dppe)(μ-CO)₃(CO)₆, **2b** (41.5 mg, 64%, mp 160 °C dec). Analytical data for **2b**: IR (c-C₆H₁₂) 2045 (w), 2025 (m), 2001 (vs), 1984 (m, br), 1970 (m), 1952 (m), 1913 (m), 1863 (w), 1817 (m, br) cm⁻¹; ¹H NMR (CDCl₃) δ 7.53–7.06 (m, 20H, C₆H₅), 4.65 (s, 5H, C₅H₅), 2.00 (s, 2H, CH₂); ¹³C NMR (CDCl₃) δ 211.13 (CO), 133.43–127.63 (C₆H₅), 81.26 (C₅H₅), 23.81 (CH₂); ³¹P NMR (CDCl₃) δ –30.20 (Ir–P, 230 K); FAB MS 1476 ([M]⁺, 11), 1448 ([M – 1CO]⁺, 13), 1420 ([M–2CO]⁺, 26), 1392 ([M–3CO]⁺, 37), 1364 ([M–4CO]⁺, 47), 1336 ([M – 5CO]⁺, 42), 1308 ([M – 6CO]⁺, 100), 1280 ([M – 7CO]⁺, 90), 1231 ([M – 6CO – 1Ph]⁺, 26), 1203 ([M – 7CO – 1Ph]⁺, 21), 1175 ([M – 8CO – 1Ph]⁺, 16), 1154 ([M – 6CO – 2Ph]⁺, 21), 1126 ([M – 7CO – 2Ph]⁺, 32), 1077 ([M – 6CO –

3Ph]⁺, 29), 1061 ([M – 7CO – 2Ph – 1Cp]⁺, 47), 1049 ([M – 7CO – 3Ph]⁺, 26). Anal. Calcd: C, 32.52; H, 1.96. Found: C, 32.35; H, 1.93.

Reaction of CpWIr₃(CO)₁₁ with dppm. An orange solution of CpWIr₃(CO)₁₁ (20.0 mg, 0.0176 mmol) and dppm (6.7 mg, 0.018 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 20 h. The resultant dark red solution was evaporated to dryness. The dark red residue obtained was dissolved in CH₂Cl₂ (ca. 1 mL) and chromatographed (3 CH₂Cl₂:2 petroleum ether). Recrystallization of the only product, R_f 0.68, from CH₂Cl₂/CH₃OH afforded dark orange crystals of CpWIr₃(μ-dppm)(μ-CO)₃(CO)₆, **2c** (15.5 mg, 76%, mp 194 °C dec). Analytical data for **2c**: IR (c-C₆H₁₂) 2043 (w), 2025 (m), 2000 (vs), 1985 (s), 1966 (w, br), 1959 (w, sh), 1920 (m), 1864 (vw) cm⁻¹; ¹H NMR (CDCl₃) δ 7.40–7.25 (m, 20H, C₆H₅), 4.89 (s, 5H, C₅H₅), 3.48 (s, 2H, CH₂); ¹³C NMR (CDCl₃) δ 132.58–128.35 (C₆H₅), 82.47 (C₅H₅), 26.80 (CH₂); ³¹P NMR (CDCl₃) δ –30.83 (Ir–P, 230 K); FAB MS 1462 ([M]⁺, 17), 1434 ([M – 1CO]⁺, 43), 1406 ([M – 2CO]⁺, 17), 1378 ([M – 3CO]⁺, 100), 1350 ([M – 4CO]⁺, 20), 1322 ([M – 5CO]⁺, 30), 1294 ([M – 6CO]⁺, 60), 1266 ([M – 7CO]⁺, 43), 1238 ([M – 8CO]⁺, 7), 1217 ([M – 6CO – 1Ph]⁺, 10), 1189 ([M – 7CO – 1Ph]⁺, 10), 1152 ([M – 6CO – 1Ph – 1Cp]⁺, 14), 1140 ([M – 6CO – 2Ph]⁺, 14), 1124 ([M – 7CO – 1Ph – 1Cp]⁺, 30), 1112 ([M – 7CO – 2Ph]⁺, 14), 1075 ([M – 6CO – 2Ph]⁺, 20), 1063 ([M – 6CO – 3Ph]⁺, 20), 1047 ([M – 7CO – 2Ph – 1Cp]⁺, 20), 1035 ([M – 7CO – 3Ph]⁺, 17), 998 ([M – 6CO – 3Ph – 1Cp]⁺, 14), 986 ([M – 6CO – 4Ph]⁺, 17), 970 ([M – 7CO – 3Ph – 1Cp]⁺, 23), 958 ([M – 7CO – 4Ph]⁺, 10). Anal. Calcd: C, 31.03; H, 1.87. Found: C, 30.91; H, 1.87.

Reaction of CpWIr₃(CO)₁₁ with dppa. An orange solution of CpWIr₃(CO)₁₁ (40.0 mg, 0.0352 mmol) and dppa (13.4 mg, 0.0352 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 3 h. The resultant dark red solution was evaporated to dryness. The brownish-orange residue obtained was dissolved in CH₂Cl₂ (ca. 2 mL) and chromatographed (7 CH₂Cl₂:10 petroleum ether). Four bands were obtained, all in low yield; the second band, R_f 0.62, was recrystallized from CH₂Cl₂/CH₃OH to afford light brown crystals of CpWIr₃(μ-dppa)(μ-CO)₃(CO)₆, **2d** (7.9 mg, 15%). Analytical data for **2d**: IR (c-C₆H₁₂) 2054 (m), 2034 (w), 2007 (vs), 1991 (m, sh), 1983 (vs), 1960 (m), 1939 (vw), 1923 (m) cm⁻¹; ¹H NMR (CDCl₃) δ 8.00–7.27 (m, 20H, C₆H₅); 4.77 (s, 5H, C₅H₅); ¹³C NMR (CDCl₃) δ 202.86 (CO), 128.64–132.49, (C₆H₅), 96.63 (≡C), 82.16 (C₅H₅). Anal. Calcd: C, 32.65; H, 1.67. Found: C, 32.08; H, 1.63.

X-ray Crystallography. Crystals of compounds **2b**, **2c**, and **2d** suitable for diffraction analyses were grown by slow diffusion of methanol into dichloromethane solutions at room temperature. Unique diffractometer data sets were measured at ~295 K within the specified $2\theta_{max}$ limit ($2\theta/\theta$ scan mode; monochromatic Mo Kα radiation ($\lambda = 0.7107_3$ Å)) yielding N independent reflections. N_o of these with $I > 3\sigma(I)$ were considered "observed" and used in the full matrix/large block least squares refinements after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Conventional residuals R, R_w on $|F|$ at convergence are given, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were used, computation using the XTAL 3.2 program system[4] implemented by S. R. Hall. Pertinent results are given in the figures and tables.

Results and Discussion

Syntheses and Characterization of 2a, 2b, and 2c.
The reactions of CpWIr₃(CO)₁₁ (**1**) with PPh₃ or the bidentate phosphines dppe or dppm proceed rapidly in dichloromethane at room temperature to afford the

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Table I. Crystallographic Data for 2b, 2c, and 2d[a]

	2b	2c	2d
chem formula	$C_{40}H_{29}Ir_3O_9P_2W$	$C_{39}H_{27}Ir_3O_9P_2W \cdot$ 2CH$_3$OH	$C_{40}H_{25}Ir_3O_9P_2W$
fw	1476.1	1526.2	1472.0
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pmnb$ (No. 62)
a, Å	18.563(5)	10.748(12)	21.608(4)
b, Å	11.855(4)	22.439(5)	17.843(3)
c, Å	10.367(2)	19.886(14)	10.134(3)
α, deg	67.72(2)		
β, deg	73.54(2)	114.95(8)	
γ, deg	77.44(2)		
V, Å^3	2009	4348	3907
ρ_{calcd}, g cm^{-3}	2.44	2.33	2.51
Z	2	4	4
μ, mm^{-1}	12.9	11.9	13.3
spec size, mm	0.094 × 0.42 × 0.36	0.20 × 0.05 × 0.07	0.05 × 0.10 × 0.25
A^* (min, max)	3.1, 20.4	1.64, 2.48	1.91, 3.81
$2\theta_{max}$, deg	65	50	50
N	13 863	7553	3532
N_o	10 230	2710	2740
R	0.045	0.087	0.032
R_w	0.049	0.088	0.034

[a] *Abnormal features/variations in procedure*—**2c**. A small, inferior specimen was used in the absence of anything better; a Gaussian absorption correction was applied. In view of the weak and limited data, anisotropic thermal parameter refinement was undertaken for Ir, W, and P only; for C and O the isotropic form was used. Hydrogen atoms were not located for the solvent; O *vs* C was assigned on the basis of the refinement behavior.

monosubstituted clusters CpWIr$_3$(μ-CO)$_3$(CO)$_7$(PPh$_3$) (**2a**),[5] CpWIr$_3$(μ-dppe)(μ-CO)$_3$(CO)$_6$ (**2b**), or CpWIr$_3$(μ-dppm)(μ-CO)$_3$(CO)$_6$ (**2c**), respectively, as the major or sole reaction products in excellent yields (64–84%). The products were characterized by a combination of IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, FAB MS, and satisfactory microanalyses. Infrared spectra indicate the presence of edge-bridging carbonyl ligands in **2b** and **2c**, in contrast to the all-terminal precursor **1**. The ^{1}H and ^{13}C NMR spectra contain signals assigned to Cp and Ph groups (and methylenes for **2b** and **2c**). The ^{31}P NMR spectra have one resonance each corresponding to the presence of phosphine ligands; the ^{31}P singlets in **2b** and **2c** (δ −30.20, −30.83, respectively) are significantly upfield of that in **2a** (δ 9.19), and no evidence for ^{183}W–^{31}P coupling is evident, indicating that substitution occurs at a different Ir site in **2a** than in **2b** or **2c**. The FAB MS spectra contain molecular ions followed by sequential loss of 10 (**2a**), 7 (**2b**), or 8 (**2c**) CO ligands and then loss of Cp and Ph (**2b** and **2c**). The above data are consistent with the formulations as written, and single crystal X-ray studies were carried out to establish the precise sites of substitution. An X-ray crystallographic study of **2a** could not be satisfactorily concluded;[6] it did, however, establish the WIr$_3$ pseudotetrahedral framework, bridging carbonyls about the Ir$_3$ plane (not evident from the IR spectrum, a fact which suggests that **2a** may adopt a different structure in solution from the solid state), and a radially-coordinated phosphine. The ^{31}P NMR data provide confirmatory evidence; Shapley has assigned upfield ^{31}P signals on tetrahedral iridium clusters to axially-coordinated phosphines,[7] and the resonance for **2a** is substantially downfield from those for **2b** and **2c**.

(5) Complex **2a** has been isolated and formulated previously: McAteer, C. H.; Shapley, J. R. Unpublished results.

(6) (a) Lee, J.; Humphrey, M. G.; Byriel, K.; Kennard, C. H. Unpublished results. (b) Lee, J.; Humphrey, M. G. RACI Qld Branch Inorganic/Organic Chemistry Symposium, Rockhampton, Australia, July 1992; Poster 2.

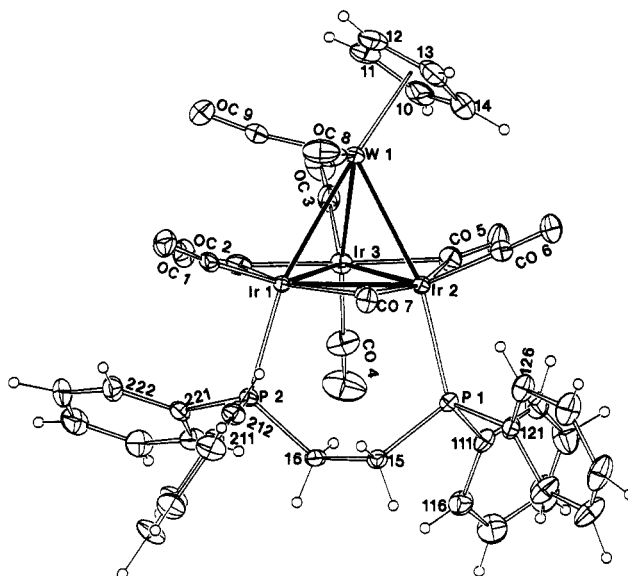(7) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607.

Figure 1. Molecular structure and atomic labeling scheme for **2b**, CpWIr$_3$(μ-dppe)(μ-CO)$_3$(CO)$_6$. Thermal envelopes (20%) are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

Figure 2. Molecular structure and atomic labeling scheme for **2c**, CpWIr$_3$(μ-dppm)(μ-CO)$_3$(CO)$_6$. Thermal envelopes (20%) are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

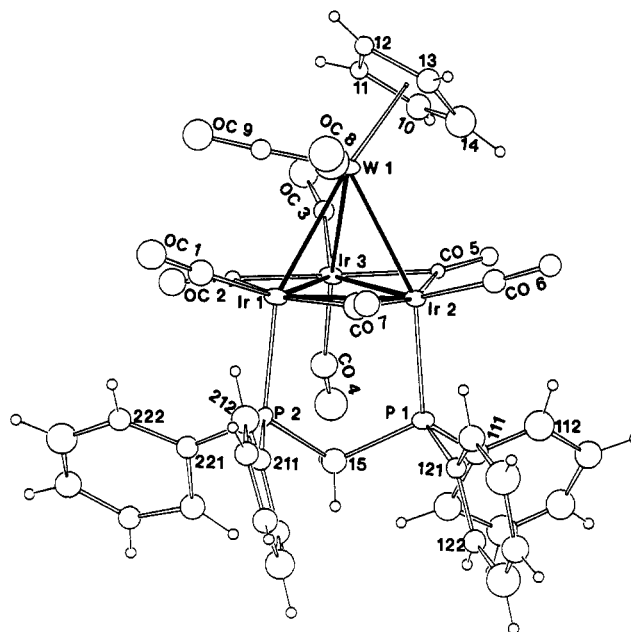**X-ray Structural Studies of 2b and 2c.** The molecular structures of **2b** and **2c** as determined by single crystal X-ray studies are consistent with the formulations given above. A summary of crystal and refinement data is found in Table I, fractional coordinates of non-hydrogen atoms are given in Table II (**2b**) and Table IV (**2c**), and selected bond distances and angles are listed in Table III (**2b**) and Table V (**2c**). ORTEP plots showing the molecular geometry and atomic numbering scheme are shown in Figure 1 (**2b**) and Figure 2 (**2c**).

Complexes **2b** and **2c** have the WIr$_3$ pseudotetrahedral framework of the precursor cluster **1** and possess η^5-cyclopentadienyl groups, three bridging carbonyls arranged about the Ir$_3$ plane, six terminal carbonyl ligands, and axially-coordinated bidentate phosphine ligands. The

Table II. Non-Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters for Complex 2b

atom	x	y	z	U(eq), Å²
Ir(1)	0.21550(2)	0.64011(3)	0.16704(3)	0.0280(1)
Ir(2)	0.33502(2)	0.77395(3)	0.03169(3)	0.0309(1)
Ir(3)	0.25211(2)	0.77700(3)	0.29673(4)	0.0394(1)
W(1)	0.35241(2)	0.56267(3)	0.27663(4)	0.0391(1)
P(1)	0.2876(1)	0.9449(2)	−0.1421(2)	0.0330(8)
P(2)	0.1142(1)	0.7630(2)	0.0779(2)	0.0306(8)
C(1)	0.1786(5)	0.4976(8)	0.1930(9)	0.039(3)
O(1)	0.1600(4)	0.4042(6)	0.2141(8)	0.061(4)
C(2)	0.1672(6)	0.6628(9)	0.365(1)	0.047(4)
O(2)	0.1214(4)	0.6226(7)	0.4681(7)	0.057(3)
C(3)	0.2651(7)	0.746(1)	0.480(1)	0.059(5)
O(3)	0.2697(6)	0.731(1)	0.5927(9)	0.109(6)
C(4)	0.1912(8)	0.932(1)	0.277(1)	0.066(6)
O(4)	0.1565(7)	1.0238(8)	0.278(1)	0.112(7)
C(5)	0.3541(6)	0.8532(9)	0.164(1)	0.054(5)
O(5)	0.3999(5)	0.9003(8)	0.1746(9)	0.078(5)
C(6)	0.4354(6)	0.7673(8)	−0.063(1)	0.050(4)
O(6)	0.4982(5)	0.7626(8)	−0.120(1)	0.085(4)
C(7)	0.2972(5)	0.6588(6)	−0.0326(9)	0.031(3)
O(7)	0.3108(4)	0.6163(5)	−0.1235(7)	0.045(3)
C(8)	0.3553(7)	0.4573(8)	0.164(1)	0.058(5)
O(8)	0.3617(5)	0.3897(7)	0.1074(9)	0.077(5)
C(9)	0.2772(6)	0.4588(9)	0.422(1)	0.056(5)
O(9)	0.2415(5)	0.3901(8)	0.512(1)	0.087(5)
C(10)	0.4307(8)	0.613(1)	0.387(2)	0.075(7)
C(11)	0.4117(8)	0.494(1)	0.467(1)	0.082(7)
C(12)	0.4426(8)	0.423(1)	0.381(2)	0.089(8)
C(13)	0.4809(7)	0.497(1)	0.243(2)	0.078(7)
C(14)	0.4737(8)	0.615(1)	0.250(2)	0.078(7)
C(15)	0.1946(5)	0.9337(7)	−0.1641(9)	0.037(3)
C(16)	0.1303(5)	0.9230(7)	−0.030(1)	0.039(3)
C(111)	0.2771(6)	1.0941(7)	−0.121(1)	0.042(4)
C(112)	0.3381(6)	1.1227(8)	−0.093(1)	0.056(5)
C(113)	0.3315(8)	1.238(1)	−0.080(2)	0.091(9)
C(114)	0.2710(9)	1.318(1)	−0.091(2)	0.091(8)
C(115)	0.2100(8)	1.291(1)	−0.117(2)	0.081(7)
C(116)	0.2121(6)	1.1779(8)	−0.133(1)	0.057(5)
C(121)	0.3413(5)	0.9744(7)	−0.326(1)	0.041(4)
C(122)	0.3317(8)	1.0883(9)	−0.429(1)	0.070(6)
C(123)	0.3685(9)	1.110(1)	−0.571(1)	0.081(7)
C(124)	0.4146(9)	1.019(1)	−0.611(1)	0.076(7)
C(125)	0.4277(7)	0.904(1)	−0.510(1)	0.065(6)
C(126)	0.3896(6)	0.8829(9)	−0.370(1)	0.052(4)
C(211)	0.0766(5)	0.7174(7)	−0.0385(9)	0.034(3)
C(212)	0.1230(6)	0.6454(8)	−0.116(1)	0.044(4)
C(213)	0.0962(7)	0.618(1)	−0.211(1)	0.059(5)
C(214)	0.0243(7)	0.664(1)	−0.228(1)	0.063(6)
C(215)	−0.0229(6)	0.734(1)	−0.155(1)	0.062(6)
C(216)	0.0041(6)	0.7635(9)	−0.058(1)	0.051(5)
C(221)	0.0317(5)	0.7777(8)	0.219(1)	0.039(3)
C(222)	−0.0096(6)	0.6778(9)	0.296(1)	0.053(4)
C(223)	−0.0678(6)	0.682(1)	0.410(1)	0.068(6)
C(224)	−0.0886(7)	0.785(1)	0.447(1)	0.075(6)
C(225)	−0.0494(7)	0.884(1)	0.375(1)	0.064(5)
C(226)	0.0104(6)	0.8815(8)	0.260(1)	0.050(4)

Table III. Important Bond Lengths (Å) and Angles (deg) for Complex 2b

Ir(1)–Ir(2)	2.7364(8)	Ir(1)–Ir(3)	2.7487(8)
Ir(2)–Ir(3)	2.7521(7)	Ir(2)–W(1)	2.8488(7)
Ir(3)–W(1)	2.8443(9)	Ir(1)–W(1)	2.9023(9)
Ir(1)–P(2)	2.299(2)	Ir(2)–P(1)	2.342(2)
Ir(1)–C(1)	1.86(1)	Ir(1)–C(2)	2.09(1)
Ir(1)–C(7)	2.156(7)	Ir(2)–C(5)	2.07(1)
Ir(2)–C(6)	1.85(1)	Ir(2)–C(7)	2.04(1)
Ir(3)–C(2)	2.10(1)	Ir(3)–C(3)	1.87(1)
Ir(3)–C(4)	1.91(1)	Ir(3)–C(5)	2.15(1)
W(1)–C(8)	1.99(1)	W(1)–C(9)	1.972(9)
W(1)–C(10)	2.37(2)	W(1)–C(11)	2.32(2)
W(1)–C(12)	2.27(1)	W(1)–C(13)	2.31(1)
W(1)–C(14)	2.38(1)	P(1)–C(15)	1.84(1)
P(2)–C(16)	1.840(7)	C(15)–C(16)	1.54(1)

Ir(2)–Ir(1)–W(1)	60.61(2)	Ir(3)–Ir(1)–W(1)	60.37(2)
Ir(2)–Ir(1)–Ir(3)	60.23(2)	Ir(1)–Ir(2)–Ir(3)	60.11(2)
Ir(1)–Ir(2)–W(1)	62.58(2)	Ir(3)–Ir(2)–W(1)	61.01(2)
Ir(1)–Ir(3)–Ir(2)	59.66(2)	Ir(1)–Ir(3)–W(1)	62.49(2)
Ir(2)–Ir(3)–W(1)	61.17(2)	Ir(2)–W(1)–Ir(3)	57.82(2)
Ir(2)–W(1)–Ir(1)	56.81(1)	Ir(3)–W(1)–Ir(1)	57.14(2)
Ir(2)–Ir(1)–P(2)	105.42(6)	Ir(3)–Ir(1)–P(2)	102.10(7)
W(1)–Ir(1)–P(2)	160.97(6)	Ir(1)–Ir(2)–P(1)	103.70(7)
Ir(3)–Ir(2)–P(1)	108.28(6)	W(1)–Ir(2)–P(1)	165.21(6)
Ir(2)–P(1)–C(15)	114.4(2)	Ir(1)–P(2)–C(16)	115.1(3)
P(1)–C(15)–C(16)	114.6(8)	P(2)–C(16)–C(15)	113.0(6)

iridium carbonyl clusters;[2b,3b,8] M–C–O angles for these carbonyls are in the range 171–178°, with no significant semibridging interactions. Complexes 2b and 2c are the first examples from the WIr₃ system with bridging carbonyls; for 2b, carbonyls bridge asymmetrically toward Ir(2), with Ir(2)–CO(b) 2.06 Å (av) and Ir(1/3)–CO(b) 2.15 Å (av). The third bridging carbonyl is symmetrically disposed between Ir(1) and Ir(3). The Ir–P (2.32 Å av (2b), 2.34 Å av (2c)) and P–CH₂ distances (1.84 Å av (2b)) are normal; once again, large errors associated with 2c preclude discussion of distances involving lighter atoms. Formal electron counting reveals 2b and 2c have 60 e, electron precise for tetrahedral clusters.

Synthesis and Characterization of 2d. Stirring an equimolar mixture of dppa and CpWIr₃(CO)₁₁ in dichloromethane afforded several products, all in low yield, of which only one has thus far been completely characterized. The second TLC band was crystallized and identified as CpWIr₃(μ-dppa)(μ-CO)₃(CO)₆ by a combination of IR and ¹H and ¹³C NMR spectra, elemental microanalyses, and a single crystal X-ray structure determination. The ¹H and ¹³C NMR spectra contain the expected Cp and Ph resonances; in the former case, integration of peaks is consistent with 1 dppa:1 CpWIr₃ core. In addition, the ¹³C NMR spectrum contains a resonance assigned to ≡C– at 96.63 ppm, suggesting that the acetylene carbons are equivalent. The linear P—C≡C—P backbone of dppa ordinarily precludes edge-bridging or chelating coordination; monodentate dppa or dppa spanning two cluster units is the preferred geometry.[9] The spectroscopic data are consistent with the presence of an unusual (μ-dppa) ligand and an X-ray study was carried out to confirm this.

WIr₃ core distances (W–Ir$_{av}$ 2.87 Å (2b), 2.85 Å (2c), Ir–Ir$_{av}$ 2.75 Å (2b), 2.73 Å (2c)) are longer than the comparable distances for 1 (W–Ir$_{av}$ 2.82 Å, Ir–Ir$_{av}$ 2.699 Å), with the longest W–Ir distance for both 2b and 2c being effectively *trans* to the Cp group and the shortest Ir–Ir bonds between the phosphine-coordinated iridiums. The cyclopentadienyl groups are inclined to a WIr₂ face and are asymmetrically disposed, with three W–C distances (av 2.30 Å (2b), 2.26 Å (2c)) significantly shorter than the two W–C distances (av 2.38 Å (2b), 2.37 Å (2c)) involving the carbons closest to the Ir–Ir vector. The precision of the structural determination of 2c does not warrant investigation of the carbonyl coordination geometry. For 2b, Ir–CO(terminal) interactions (1.84–1.91 Å) and W–CO distances (1.97–1.99 Å) are comparable to those reported in other tungsten-

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Table IV. Non-Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters for Complex 2c

atom	x	y	z	U(eq), Å^2
Ir(1)	0.2613(2)	0.2893(1)	0.6898(1)	0.035(1)
Ir(2)	0.2245(2)	0.4052(1)	0.6511(1)	0.032(1)
Ir(3)	0.2651(2)	0.3244(1)	0.5586(1)	0.035(1)
W(1)	0.0093(3)	0.3249(1)	0.5686(1)	0.038(1)
P(1)	0.455(2)	0.4326(8)	0.7202(9)	0.039(8)
P(2)	0.490(2)	0.3004(7)	0.7723(8)	0.032(7)
C(1)	0.220(5)	0.225(3)	0.728(4)	0.06(2)
O(1)	0.187(4)	0.183(2)	0.754(3)	0.08(2)
C(2)	0.291(6)	0.245(2)	0.603(3)	0.02(1)
O(2)	0.328(5)	0.194(2)	0.600(2)	0.07(1)
C(3)	0.179(6)	0.303(3)	0.463(3)	0.04(2)
O(3)	0.137(5)	0.278(2)	0.405(2)	0.08(2)
C(4)	0.466(8)	0.330(3)	0.566(4)	0.06(2)
O(4)	0.554(6)	0.341(3)	0.561(3)	0.09(2)
C(5)	0.212(5)	0.414(2)	0.548(3)	0.019(6)
O(5)	0.184(4)	0.453(2)	0.500(2)	0.03(1)
C(6)	0.147(4)	0.471(2)	0.655(3)	0.05(2)
O(6)	0.085(4)	0.517(2)	0.658(2)	0.05(1)
C(7)	0.221(7)	0.361(3)	0.733(4)	0.07(2)
O(7)	0.181(4)	0.373(2)	0.784(2)	0.06(1)
C(8)	−0.05(1)	0.317(4)	0.658(5)	0.11(4)
O(8)	−0.087(6)	0.314(3)	0.700(3)	0.11(2)
C(9)	0.011(5)	0.250(2)	0.565(2)	0.04(2)
O(9)	0.009(5)	0.194(2)	0.561(2)	0.08(2)
C(10)	−0.087(7)	0.370(3)	0.448(4)	0.06(2)
C(11)	−0.143(6)	0.314(2)	0.449(3)	0.03(1)
C(12)	−0.225(6)	0.319(3)	0.493(3)	0.03(1)
C(13)	−0.191(7)	0.380(3)	0.520(4)	0.05(2)
C(14)	−0.101(8)	0.411(4)	0.495(4)	0.08(3)
C(15)	0.570(7)	0.363(3)	0.750(4)	0.06(2)
C(111)	0.533(7)	0.479(3)	0.669(4)	0.05(2)
C(112)	0.466(8)	0.525(4)	0.631(5)	0.08(3)
C(113)	0.528(8)	0.569(3)	0.598(4)	0.07(2)
C(114)	0.649(9)	0.552(4)	0.604(4)	0.08(3)
C(115)	0.713(9)	0.508(4)	0.639(5)	0.08(3)
C(116)	0.665(8)	0.461(4)	0.672(4)	0.07(2)
C(121)	0.499(6)	0.473(3)	0.803(3)	0.04(2)
C(122)	0.632(7)	0.500(3)	0.842(4)	0.05(2)
C(123)	0.67(1)	0.534(4)	0.907(5)	0.10(3)
C(124)	0.579(8)	0.541(3)	0.929(4)	0.07(2)
C(125)	0.44(1)	0.520(4)	0.904(5)	0.10(3)
C(126)	0.406(7)	0.484(3)	0.837(4)	0.06(2)
C(211)	0.529(6)	0.309(3)	0.873(3)	0.04(2)
C(212)	0.433(7)	0.293(3)	0.895(4)	0.07(2)
C(213)	0.465(7)	0.304(3)	0.971(4)	0.05(2)
C(214)	0.579(7)	0.331(3)	1.019(4)	0.05(2)
C(215)	0.683(8)	0.348(3)	0.996(4)	0.08(2)
C(216)	0.655(6)	0.337(3)	0.921(4)	0.05(2)
C(221)	0.594(7)	0.239(3)	0.770(3)	0.04(2)
C(222)	0.563(6)	0.178(3)	0.771(3)	0.04(2)
C(223)	0.638(9)	0.132(3)	0.761(4)	0.08(3)
C(224)	0.745(7)	0.143(3)	0.749(4)	0.06(2)
C(225)	0.789(6)	0.198(3)	0.752(3)	0.05(2)
C(226)	0.728(7)	0.251(3)	0.765(4)	0.05(2)
O(01)	0.02(1)	0.411(5)	0.925(7)	0.27(5)
C(01)	−0.04(1)	0.376(4)	0.860(5)	0.11(3)
O(01′)	0.04(2)	0.501(9)	0.91(1)	0.4(1)
C(01′)	0.00(2)	0.540(7)	0.844(9)	0.22(7)

Table V. Important Bond Lengths (Å) and Angles (deg) for Complex 2c

Ir(1)–Ir(2)	2.694(4)	Ir(1)–W(1)	2.877(5)
Ir(1)–Ir(3)	2.743(5)	Ir(2)–W(1)	2.844(4)
Ir(2)–Ir(3)	2.746(4)	Ir(3)–W(1)	2.838(5)
Ir(2)–P(1)	2.35(2)	Ir(1)–P(2)	2.33(1)
Ir(1)–C(1)	1.77(6)	Ir(1)–C(2)	2.14(6)
Ir(1)–C(7)	1.97(8)	Ir(2)–C(5)	2.01(6)
Ir(2)–C(6)	1.72(5)	Ir(2)–C(7)	1.92(8)
Ir(3)–C(2)	1.96(6)	Ir(3)–C(3)	1.79(6)
Ir(3)–C(4)	2.10(9)	Ir(3)–C(5)	2.08(5)
W(1)–C(8)	2.1(1)	W(1)–C(9)	1.69(5)
W(1)–C(10)	2.40(7)	W(1)–C(11)	2.25(5)
W(1)–C(12)	2.33(5)	W(1)–C(13)	2.32(7)
W(1)–C(14)	2.42(8)	P(1)–C(15)	1.92(7)
P(2)–C(15)	1.80(8)		

Ir(2)–Ir(1)–W(1)	61.30(9)	Ir(2)–Ir(1)–Ir(3)	60.7(1)
Ir(3)–Ir(1)–W(1)	60.6(1)	Ir(1)–Ir(2)–Ir(3)	60.6(1)
Ir(1)–Ir(2)–W(1)	62.5(1)	Ir(3)–Ir(2)–W(1)	61.0(1)
Ir(1)–Ir(3)–Ir(2)	58.8(1)	Ir(1)–Ir(3)–W(1)	62.0(1)
Ir(2)–Ir(3)–W(1)	61.2(1)	Ir(1)–W(1)–Ir(2)	56.2(1)
Ir(1)–W(1)–Ir(3)	57.4(1)	Ir(2)–W(1)–Ir(3)	57.8(1)
Ir(1)–Ir(2)–P(1)	95.4(4)	Ir(3)–Ir(2)–P(1)	97.9(5)
W(1)–Ir(2)–P(1)	154.5(5)	Ir(3)–Ir(1)–P(2)	101.7(5)
W(1)–Ir(1)–P(2)	154.6(4)	Ir(2)–Ir(1)–P(2)	94.7(4)
Ir(2)–P(1)–C(15)	111(2)	Ir(1)–P(2)–C(15)	113(2)
P(1)–C(15)–P(2)	113(4)		

Table VI. Non-Hydrogen Atom Coordinates and Equivalent Isotropic Displacement Parameters for Complex 2d

atom	x	y	z	U(eq), Å^2
Ir(1)	0.31450(2)	0.37925(2)	0.19617(4)	0.0282(1)
Ir(2)	1/4	0.25861(3)	0.10621(6)	0.0330(2)
W(1)	1/4	0.39583(3)	−0.04469(6)	0.0318(2)
P(1)	0.3464(1)	0.3523(1)	0.4124(3)	0.0309(8)
C(1)	1/4	0.4615(7)	0.250(1)	0.030(4)
C(2)	0.3790(5)	0.4428(6)	0.152(1)	0.041(4)
O(1)	1/4	0.5227(5)	0.290(1)	0.042(4)
O(2)	0.4194(4)	0.4803(5)	0.122(1)	0.071(4)
C(3)	0.3490(6)	0.2831(6)	0.121(1)	0.047(4)
O(3)	0.3924(4)	0.2485(4)	0.0890(9)	0.060(3)
C(4)	1/4	0.1949(8)	0.256(2)	0.048(6)
O(4)	1/4	0.1635(6)	0.352(1)	0.069(5)
C(5)	1/4	0.1824(9)	−0.020(2)	0.053(6)
O(5)	1/4	0.1375(7)	−0.103(1)	0.092(6)
C(6)	0.1886(5)	0.3311(6)	−0.134(1)	0.043(4)
O(6)	0.1535(4)	0.2966(5)	−0.1932(8)	0.066(3)
C(7)	0.2823(5)	0.5234(5)	−0.040(1)	0.044(4)
C(8)	0.3034(6)	0.4886(6)	−0.159(1)	0.058(5)
C(9)	1/4	0.4671(9)	−0.230(2)	0.067(8)
C(10)	0.2786(4)	0.3364(5)	0.5013(9)	0.033(3)
C(11)	0.3937(5)	0.2704(5)	0.438(1)	0.043(4)
C(12)	0.3769(6)	0.2133(6)	0.524(1)	0.054(4)
C(13)	0.4172(8)	0.1547(7)	0.544(1)	0.073(6)
C(14)	0.4721(8)	0.1529(8)	0.480(2)	0.083(7)
C(15)	0.4897(6)	0.2065(8)	0.393(2)	0.072(6)
C(16)	0.4503(6)	0.2659(6)	0.371(1)	0.054(4)
C(21)	0.3874(5)	0.4256(5)	0.503(1)	0.037(3)
C(22)	0.3754(6)	0.5002(6)	0.476(1)	0.054(4)
C(23)	0.4062(6)	0.5570(6)	0.549(1)	0.057(5)
C(24)	0.4493(6)	0.5363(7)	0.641(1)	0.053(4)
C(25)	0.4613(6)	0.4629(7)	0.667(1)	0.053(4)
C(26)	0.4311(5)	0.4073(6)	0.600(1)	0.046(4)

X-ray Structural Study of 2d. The molecular structure of 2d was determined by a single crystal X-ray study. A summary of crystal refinement data is given in Table I, fractional coordinates of non-hydrogen atoms are listed in Table VI, and selected bond distances and angles are collected in Table VII. An ORTEP plot showing the molecular geometry and atomic numbering scheme for 2d is shown in Figure 3. The molecule with crystallographic *m* symmetry has a WIr$_3$ pseudotetrahedral framework, with ligand distribution as in 2b and 2c. The WIr$_3$ core distances (W–Ir$_{av}$ 2.85 Å, Ir–Ir$_{av}$ 2.74 Å) are comparable to 2b and 2c; as with 2b and 2c, the longest W–Ir distance is that *trans* to the Cp group, but by contrast, the longest Ir–Ir bond is that between the phosphine-coordinated

iridiums. Unlike 2b and 2c, the cyclopentadienyl ligand is inclined to the WIr$_2$ face containing the two P-coordinated iridiums. As with 2b and 2c, three W–C(Cp) distances (av 2.31 Å) are significantly shorter than the two W–C(Cp) distances (av 2.38 Å) involving the carbons closest to the Ir–Ir bond. Ir–CO(t) (1.85–1.91(1) Å) and W–CO distances (1.98(1) Å) are comparable to those of 2b, with angles M–C–O 174-178°. For 2d, the carbonyls CO(3) bridge asymmetrically between Ir(1) and the non-phosphine-ligated Ir(2), unlike 2b, with Ir(2)–CO(3) 2.19(1) Å and Ir(1)–CO(3) 2.02(1) Å; the third carbonyl CO(1) lies
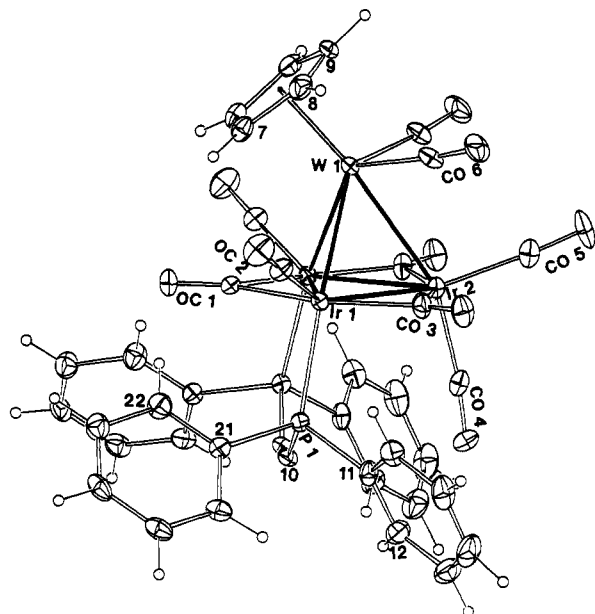
Figure 3. Molecular structure and atomic labeling scheme for **2d**, CpWIr₃(μ-dppa)(μ-CO)₃(CO)₆. Thermal envelopes (20%) are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

Table VII. Important Bond Lengths (Å) and Angles (deg) for Complex 2d[a]

Ir(1)–Ir(2)	2.7216(7)	Ir(1)–W(1)	2.8262(9)
Ir(1)–Ir(1′)	2.7874(8)	Ir(2)–W(1)	2.8867(9)
Ir(1)–P(1)	2.347(3)	Ir(1)–C(1)	2.10(1)
Ir(1)–C(2)	1.85(1)	Ir(1)–C(3)	2.02(1)
Ir(2)–C(3)	2.19(1)	Ir(2)–C(4)	1.90(2)
Ir(2)–C(5)	1.87(2)	W(1)–C(6)	1.98(1)
W(1)–C(7)	2.38(1)	W(1)–C(8)	2.33(1)
W(1)–C(9)	2.27(2)	P(1)–C(10)	1.74(1)
C(10)–C(10′)	1.23(1)		
Ir(2)–Ir(1)–W(1)	62.68(2)	Ir(2)–Ir(1)–Ir(1′)	59.20(1)
W(1)–Ir(1)–Ir(1′)	60.45(2)	Ir(1)–Ir(2)–W(1)	60.43(2)
Ir(1)–Ir(2)–Ir(1′)	61.60(2)	Ir(1)–W(1)–Ir(1′)	59.09(2)
Ir(1)–W(1)–Ir(2)	56.89(2)	Ir(2)–Ir(1)–P(1)	107.52(7)
W(1)–Ir(1)–P(1)	166.56(7)	P(1)–Ir(1)–Ir(1′)	107.08(7)
Ir(1)–P(1)–C(10)	105.6(3)	P(1)–C(10)–C(10′)	147.2(8)

[a] Primed atoms are reflection related.

in the mirror plane and bridges Ir(1,1′) symmetrically (2 × 2.10(1) Å). As with **2a**, complex **2d** provides no evidence for bridging carbonyls in the IR spectrum and may adopt an all-terminal carbonyl geometry in solution.

The unusual feature of the structure of **2d** is the edge-bridging dppa ligand. The Ir—P (2.347(3) Å), P—C(10)-(sp) (1.74(1) Å), and C≡C (1.23(1) Å) distances are as expected; however, the constraints of the six-membered ring force the strained ∠P—C≡C 147.2(8)° geometry on the linear dppa precursor. This is only the second example of an unsupported μ-dppa ligand to be structurally characterized; in Re₃(μ-H)₃(μ-dppa)(CO)₁₀, similar distortion with ∠P—C≡C of 150 and 152° was observed, with the dppa ligand spanning a long (3.303 Å)Re—Re bond.[10]

In **2d**, the dppa ligand induces some Ir—Ir bond lengthening (2.7874(8) Å, cf. 2.7364(8) Å for **2b**) to relieve strain.

Discussion. The reactions of the tetrahedral homometallic cluster Ir₄(CO)₁₂ (**3**) with phosphines have been intensively investigated, with studies concentrating on stereochemistry, fluxionality, and reaction kinetics.[7,11] The isoelectronic bimetallic cluster CpWIr₃(CO)₁₁ (**1**) is related to **3** by conceptual replacement of one Ir(CO)₃ unit in **3** with an isolobal[12] CpW(CO)₂ moiety; comparisons between the two systems are useful. Thus, substitution of carbonyl ligands in **3** by phosphine affords mono- or di-substituted products in 20–70% yields, in reactions requiring elevated temperatures (80–120 °C). By contrast, substitution reactions on **1** proceed at room temperature in minutes to afford monosubstituted products in excellent yields. In both the homometallic and bimetallic systems, substitution of carbonyl by phosphine converts the all-terminal carbonyl ligand geometry to one in which an Ir₃ plane has three edge-bridging carbonyl groups; substitution by PPh₃ and bidentate phosphines occurs at these iridiums in both systems. Ir₄(CO)₁₁(PPh₃) is axially-substituted, the preferred geometry in monosubstituted tetrahedral clusters.[1b] By contrast, **2a** is radially-substituted, an uncommon geometry in tetrahedral clusters although examples such as RuRh₃H(CO)₁₁(PMe₂Ph) are known.[1b] Substitution on **3** by dppm or dppe proceeds to afford diaxially-coordinated clusters;[11j] similarly, bidentate phosphine substitution on **1** gives diaxially-coordinated products.

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