

Ortho Phosphorylation of PPh₃ To Give a Diphosphine and Formation of a “Butterfly” Structure on a Tetrairidium Framework

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Received September 7, 2004

A brief thermolysis of the bis-phosphine-substituted tetrairidium cluster Ir₄(CO)₁₀(PPh₃)₂ (**1**) in chlorobenzene (CB) converts it rapidly to the diphosphine cluster Ir₄(CO)₇(μ-CO)₃{κ²-Ph₂P(o-C₆H₄)PPh₂} (**2**) in 53% yield, providing evidence for ortho phosphorylation at the tetrairidium cluster framework. Treatment of **2** with excess C₆₀ affords the “butterfly” Ir₄-C₆₀ complex Ir₄(CO)₆(μ-CO){μ₃-κ²-Ph₂P(o-C₆H₄)P(η¹-o-C₆H₄)}(μ₃-η²:η²:η²-C₆₀) (**3**) in 71% yield. Interestingly, compound **3** can be prepared directly from the thermolysis of **1** with excess C₆₀ in moderate yield (52%). Compounds **2** and **3** have been characterized by microanalysis, spectroscopy, and single-crystal X-ray diffraction studies. A molecular structure determination reveals that complex **2** adopts a regular tetrahedral geometry with three edge-bridging CO groups around the basal triangle and a diphosphine κ²-Ph₂P(o-C₆H₄)PPh₂ ligand chelating one of the basal iridium atoms. In contrast, complex **3** possesses a “butterfly” geometry in which the C₆₀ ligand is coordinated to the lower wing of the “butterfly” by an arene type μ₃-η²:η²:η²-C₆₀ bonding mode. One unique feature of **3** is the presence of both ortho phosphorylated and ortho-metalated phenyl rings forming five-membered [Ir-P-C-C-P] and [Ir-Ir-P-C-C] metallocycles joined in a spiro union at the iridium-iridium-bridged phosphorus atom. A crossover experiment confirms that the conversion of **1** to **2** is intramolecular. Plausible reaction pathways for the formation of **2** and **3** are proposed.

Introduction

The extensive use of [60]fullerene, the most abundant member of the fullerene family, as a ligand in organometallic chemistry has been attributed to its pivotal role in material science, owing to its unique electronic, optical, and magnetic properties.¹ In particular, the interaction of a carbon cluster such as C₆₀ with metal clusters has been a topic of great interest in exohedral metallofullerene chemistry,² because C₆₀-metal cluster complexes have a direct analogy to carbon nanotubes functionalized with metal nanoparticles.³ Furthermore, C₆₀-metal cluster complexes exhibit very strong electronic communication between C₆₀ and metal-cluster centers that can be fine-tuned by ligands attached to the metal atoms.^{2a}

Metal clusters substituted with donor ligands are commonly employed for the syntheses of C₆₀-metal cluster complexes, since C₆₀ acts as an electron-withdrawing ligand. In our previous work, we examined the

reactions of C₆₀ with phosphine-substituted metal clusters such as Ir₄(CO)₉(PPh₃)₃,⁴ Ir₄(CO)₈(PMe₃)₄,⁵ and Rh₆(CO)₁₂(dppm)₂.⁶ As an extension of our studies on the chemistry of C₆₀-metal cluster complexes, we examined the reaction between Ir₄(CO)₁₀(PPh₃)₂ (**1**) and C₆₀. Herein we report the full details of synthesis and characterization of Ir₄(CO)₇(μ-CO)₃{κ²-Ph₂P(o-C₆H₄)-PPh₂} (**2**) formed by ortho phosphorylation of PPh₃ and Ir₄(CO)₆(μ-CO){μ₃-κ²-Ph₂P(o-C₆H₄)P(η¹-o-C₆H₄)}(μ₃-η²:η²:η²-C₆₀) (**3**) by stabilization of the “butterfly” structure from the reaction of tetrahedral **1** with C₆₀, as shown in Scheme 1.

Results and Discussion

Synthesis and Characterization of 2 and 3. Thermolysis of Ir₄(CO)₁₀(PPh₃)₂ (**1**) in chlorobenzene (CB) at

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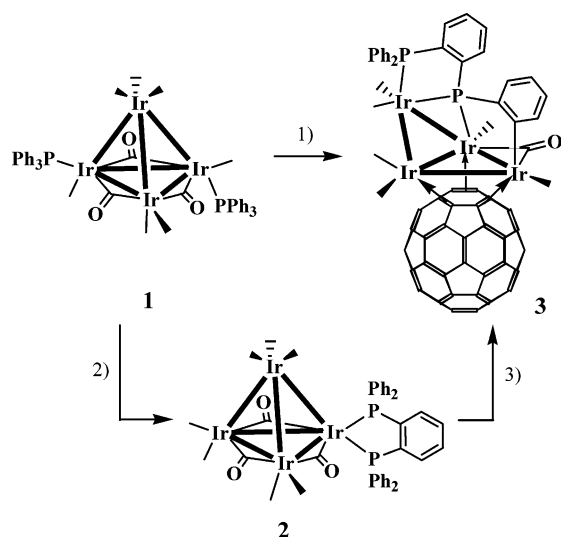
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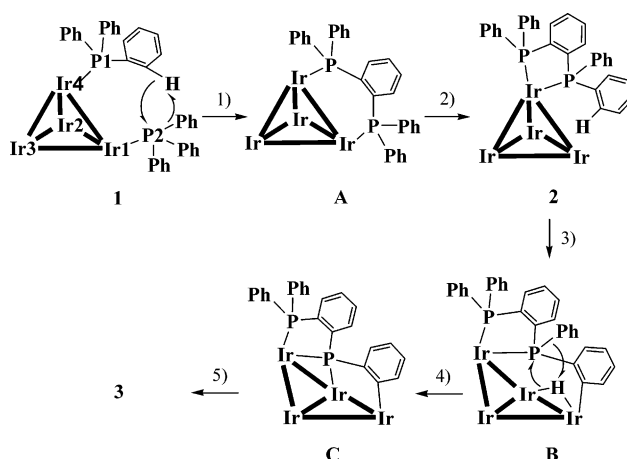
Scheme 1^a

^a Legend: (1) 2 equiv of C_{60} , $\text{C}_6\text{H}_5\text{Cl}$, 132°C , 2 h; (2) $\text{C}_6\text{H}_5\text{Cl}$, 132°C , 10 min; (3) 2 equiv of C_{60} , $\text{C}_6\text{H}_5\text{Cl}$, 132°C , 2 h. Terminal carbonyl ligands have been omitted for clarity.

132°C for ca. 10 min, followed by workup and chromatographic separation, afforded a major compound containing a diphosphine ligand, $\text{Ir}_4(\text{CO})_7(\mu\text{-CO})_3\{\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{PPh}_2\}$ (2), in 53% yield, together with a minor and unidentified band. When 2 was treated with 2 equiv of C_{60} in refluxing CB for 2 h, the $\text{Ir}_4\text{-C}_{60}$ derivative $\text{Ir}_4(\text{CO})_6(\mu\text{-CO})_3\{\mu_3\text{-}\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{P}(\eta^1\text{-o-C}_6\text{H}_4))(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60})$ (3) was obtained in high yield (71%) as a black solid. Thermolysis of 2 without C_{60} under similar conditions resulted only in extensive decomposition. Interestingly, the reaction of 1 with C_{60} produced 3 directly in moderate yield (52%), after the reaction mixture was refluxed in CB for 2 h. This implies that 2 is an intermediate for product 3. The synthetic details for 2 and 3 are given in Scheme 1.

The IR spectra of 2 and 3 exhibit two bridging CO bands at 1855 and 1799 cm^{-1} and one band at 1827 cm^{-1} , respectively, consistent with structural assignments (vide infra). The ^1H NMR spectrum of 2 shows multiplets at δ 7.56, 7.51, and 7.35–7.24 assigned to aromatic protons. The signals at δ 7.56 and 7.51 correspond to four *o*-phenylene group protons, and the signals at δ 7.35–7.24 are assigned to the phenyl group protons. Similar chemical shifts for the four protons of the *o*-phenylene bridge (ca. δ 7.58) are observed in $\text{Pd}\{\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{PPh}_2\}\text{Br}_2$ (4).⁷ The ^1H NMR spectrum of 3 shows multiplets in the aromatic region at δ 7.69–7.36 assigned to phenyl group protons. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2 shows a singlet at δ 23.2 for the two magnetically equivalent phosphorus atoms of the diphosphine ligand (cf. δ 64.2 in 4).⁷ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3 contains two singlets at δ 182.2 and 25.1 for the two phosphorus atoms. The former is assigned to the bridging phosphorus atom, commonly observed in the downfield region (δ 130–300).⁴ The singlet at δ 25.1 is consistent with a terminal phosphorus atom bonded to an iridium center (δ –30 to +70).⁴ Unfortunately, the mass spectrum of 3 could not be obtained.

A crossover experiment was carried out employing $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$ (1) and $\text{Ir}_4(\text{CO})_{10}(\text{P}(p\text{-tol})_3)_2$ (*p*-tol =

Scheme 2^a

^a Legend: (1) ortho phosphorylation, $-\text{C}_6\text{H}_6$; (2) rearrangement of the diphosphine ligand; (3) ortho metalation; (4) $-\text{C}_6\text{H}_6$; (5) -3 CO , $+\text{C}_{60}$. Carbonyl and C_{60} ligands have been omitted for clarity.

p- $\text{C}_6\text{H}_4\text{CH}_3$) in a 1:1 ratio, but crossover products, $\text{Ir}_4(\text{CO})_7(\mu\text{-CO})_3(\text{PPh}_3)_2\{\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{P}(p\text{-tol})_2\}$ and $\text{Ir}_4(\text{CO})_7(\mu\text{-CO})_3(\text{PPh}_3)_2\{\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_3\text{CH}_3)\text{P}(p\text{-tol})_2\}$, were not detected. This observation suggests that the transformation $1 \rightarrow 2$ is intramolecular. From this mechanistic data, plausible reaction pathways for the conversion $1 \rightarrow 2 \rightarrow 3$ are proposed in Scheme 2. The first step is an ortho phosphorylation in 1, which involves activation of C–H and P–C bonds of the two phenyl groups on the P1 and P2 atoms, respectively, and subsequent elimination of benzene to form the proposed intermediate A with the bridging diphosphine $\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{PPh}_2$. The second step is a rearrangement of the bridging diphosphine ligand from Ir1 to Ir4 to give the isolated intermediate 2. A similar structure is preceded in $\text{Ir}_4(\text{CO})_{10}(1,2\text{-bis(dimethylarsino)benzene})$.⁸ Ortho metalation of a phenyl group on P2 in 2 results in the rupture of the Ir1–Ir4 bond to form the proposed hydrido “butterfly” intermediate B (62 valence electrons (VE)); this conversion was previously reported in an Ir_4 cluster.⁴ Binuclear reductive elimination of C_6H_6 at the Ir4 and P2 centers in B induces coordination of the P2 atom to the Ir2 center in the proposed intermediate C. The final product 3 is produced by the loss of three carbonyl groups from C followed by $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$ coordination to one wing of the “butterfly”.

In the transformation $1 \rightarrow 2 \rightarrow 3$, two PPh_3 ligands are converted to the diphosphine $\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{PPh}_2$ and further to a $\mu_3\text{-}\kappa^2\text{-Ph}_2\text{P(o-C}_6\text{H}_4)\text{P}(\eta^1\text{-o-C}_6\text{H}_4)$ unit on the Ir_4 framework by successive ortho phosphorylation and ortho metalation, as illustrated in Scheme 2. Synthesis of phosphine ligands with $\text{P}(\text{C})_n\text{-P}$ and $\text{P}(\text{C})_n\text{-P}(\text{C})_n\text{-P}$ donor atom sequences is of special interest because of their ability to bridge metal–metal bonds and, thus, to stabilize oligometallic or metal cluster complexes. Such phosphine ligands have previously been prepared by tedious multistep organic syn-

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Table 1. Crystal and Structural Determination Data for 2 and 3

	2	3·CS ₂
formula	C ₄₀ H ₂₄ Ir ₄ O ₁₀ P ₂	C ₉₁ H ₁₈ Ir ₄ O ₇ P ₂ ·CS ₂
fw	1495.33	2129.92
syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	10.6813(9)	16.301(3)
b, Å	12.406(1)	24.121(5)
c, Å	16.709(1)	17.570(4)
α, deg	75.039(1)	90
β, deg	85.648(2)	107.518(4)
γ, deg	70.834(2)	90
V, Å ³	2020.4(3)	6588(2)
Z	2	4
D _{calcd} , Mg m ⁻³	2.458	2.147
temp, K	293(2)	293(2)
λ(Mo Kα), Å	0.71073	0.71073
μ, mm ⁻¹	13.267	8.232
θ _{min} , θ _{max} , deg	1.92, 27.99	1.49, 25.54
R _F ^a	0.0540	0.0813
R _w ^b	0.1206	0.2001
GOF	1.082	1.141

^a $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

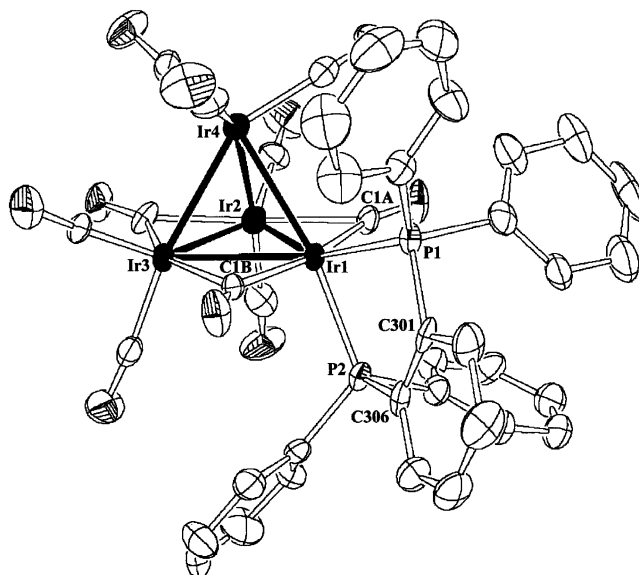
Table 2. Selected Interatomic Distances (Å) and Angles (deg) with Esd's for 2

Bond Distances			
Ir(1)–Ir(2)	2.7715(6)	Ir(1)–Ir(3)	2.7683(6)
Ir(2)–Ir(3)	2.6974(6)	Ir(2)–Ir(4)	2.7175(6)
Ir(3)–Ir(4)	2.7099(6)	Ir(1)–Ir(4)	2.7500(6)
Ir(1)–P(1)	2.287(3)	Ir(1)–P(2)	2.296(3)
P(1)–C(301)	1.85(1)	P(2)–C(306)	1.82(1)
C(301)–C(306)	1.37(2)		
Bond Angles			
Ir(4)–Ir(1)–Ir(3)	58.82(1)	Ir(4)–Ir(1)–Ir(2)	58.97(1)
Ir(3)–Ir(1)–Ir(2)	58.28(1)	Ir(3)–Ir(2)–Ir(4)	60.06(2)
Ir(3)–Ir(2)–Ir(1)	60.80(1)	Ir(4)–Ir(2)–Ir(1)	60.12(2)
Ir(2)–Ir(3)–Ir(4)	60.34(2)	Ir(2)–Ir(3)–Ir(1)	60.92(2)
Ir(4)–Ir(3)–Ir(1)	60.25(2)	Ir(3)–Ir(4)–Ir(2)	59.60(2)
Ir(3)–Ir(4)–Ir(1)	60.93(1)	Ir(2)–Ir(4)–Ir(1)	60.91(2)
P(1)–Ir(1)–P(2)	82.5(1)	P(1)–Ir(1)–Ir(4)	108.90(7)
P(2)–Ir(1)–Ir(4)	168.32(7)	P(1)–Ir(1)–Ir(3)	144.24(7)
P(2)–Ir(1)–Ir(3)	110.40(7)	P(1)–Ir(1)–Ir(2)	148.69(7)
P(2)–Ir(1)–Ir(2)	112.54(7)	Ir(1)–P(1)–C(301)	105.7(3)
Ir(1)–P(1)–C(306)	106.1(4)		

thesis.⁹ Instances of phosphine coupling to form a diphosphine on a metallic framework are rare, with two examples for Pd⁷ and Ir⁴ having been previously reported.

X-ray Crystal Structures of 2 and 3. Details of the crystallographic data for **2** and **3** are summarized in Table 1. Selected interatomic distances and angles of **2** and **3** are listed in Tables 2 and 3, respectively.

The molecular structure of **2** is shown in Figure 1. Compound **2** adopts a tetrahedral geometry (60 VE) containing 10 carbonyl groups and one diphosphine ligand. The basal triangle, Ir(1)–Ir(2)–Ir(3), has two long bonds (Ir(1)–Ir(2) = 2.7715(6) Å and Ir(1)–Ir(3) = 2.7683(6) Å) and one short bond (Ir(2)–Ir(3) = 2.6974(6) Å). However, the average iridium–iridium distance of 2.736(6) Å is comparable to that found in previously reported tetrahedral complexes (2.739 Å).¹⁰ The basal triangle accommodates three bridging CO groups. Furthermore, the Ir(1) atom is chelated by the κ^2 -P(*o*-C₆H₄)P ligand, a four-electron donor. The P(1)

**Figure 1.** Molecular structure of **2**.**Table 3. Selected Interatomic Distances (Å) and Angles (deg) with Esd's for 3**

Bond Distances			
Ir(1)–Ir(2)	2.759(1)	Ir(1)–Ir(3)	2.845(1)
Ir(2)–Ir(3)	2.888(1)	Ir(2)–Ir(4)	2.789(1)
Ir(3)–Ir(4)	2.757(1)	Ir(4)–P(1)	2.320(5)
Ir(4)–P(2)	2.272(5)	Ir(1)–C(1)	2.30(2)
Ir(1)–C(2)	2.26(2)	Ir(2)–C(3)	2.16(2)
Ir(2)–C(4)	2.25(2)	Ir(3)–C(5)	2.20(2)
Ir(3)–C(6)	2.18(2)	P(1)–C(301)	1.85(2)
P(2)–C(401)	1.80(2)	P(2)–C(306)	1.83(2)
C(301)–C(306)	1.36(3)	C(401)–C(406)	1.44(3)
C(1)–C(2)	1.43(3)	C(1)–C(6)	1.47(2)
C(2)–C(3)	1.51(2)	C(3)–C(4)	1.45(3)
C(4)–C(5)	1.48(2)	C(5)–C(6)	1.48(2)
Ir(1)–C(406)	2.07(2)		
Bond Angles			
Ir(2)–Ir(1)–Ir(3)	62.01(3)	Ir(3)–Ir(2)–Ir(4)	58.07(3)
Ir(3)–Ir(2)–Ir(1)	60.47(3)	Ir(4)–Ir(2)–Ir(1)	109.15(3)
Ir(2)–Ir(3)–Ir(4)	59.18(3)	Ir(2)–Ir(3)–Ir(1)	57.52(3)
Ir(4)–Ir(3)–Ir(1)	107.60(3)	Ir(2)–Ir(4)–Ir(3)	62.75(3)
P(2)–Ir(4)–P(1)	84.3(2)	P(2)–Ir(4)–Ir(3)	83.4(1)
P(1)–Ir(4)–Ir(3)	166.0(1)	C(306)–P(2)–Ir(2)	114.1(6)
C(401)–P(2)–Ir(4)	131.1(7)	C(306)–P(2)–Ir(4)	110.7(6)
C(301)–P(1)–Ir(4)	108.7(6)	C(406)–C(401)–P(2)	120(1)
C(301)–C(306)–P(2)	118(1)	C(306)–C(301)–P(1)	118(2)

atom is lying almost in the basal plane, whereas P(2) lies below the plane, forming the five-membered metallacycle Ir(1)–P(1)–C(301)–C(306)–P(2). Overall structural features of **2** are similar to those of Ir₄(CO)₁₀(1,2-bis(dimethylarsino)benzene).⁸

The molecular structure of **3** is depicted in Figure 2. Compound **3** reveals a “butterfly” geometry (62 VE) to which seven carbonyl groups (six terminal and one bridging), a μ_3 - η^2 : η^2 : η^2 -C₆₀ group, and a bridging diphosphine ligand are coordinated. The bond length of the Ir(2)–Ir(3) “hinge” is 2.888(1) Å, relatively longer than the Ir–Ir bond distances in the two “wings”. However, the average iridium–iridium bond distance of 2.808(1) Å is comparable to those observed in other “butterfly” tetrairidium clusters.¹¹ The Ir(1)–Ir(2) edge is asymmetrically bridged by a carbonyl ligand. The P(1) atom

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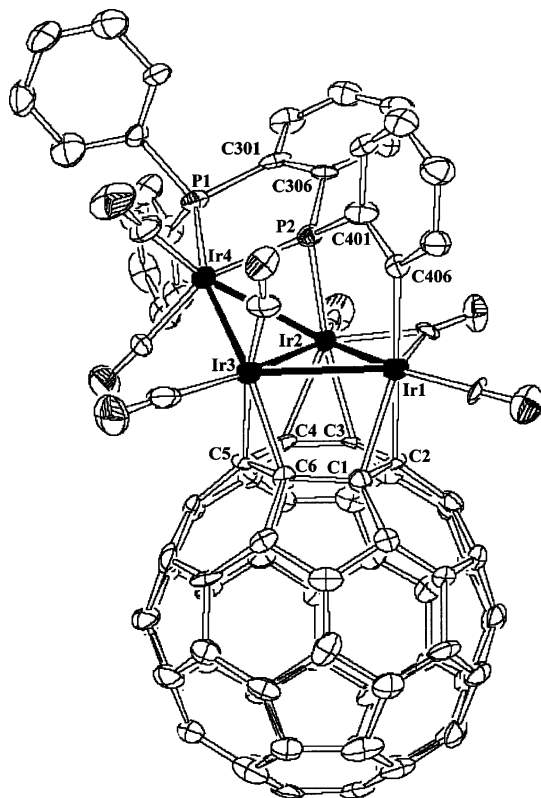


Figure 2. Molecular structure of **3**.

with two phenyl groups is axially coordinated to the Ir(4) atom. The P(2) atom is bridging the Ir(2) and Ir(4) edge, and a phenyl group on the P(2) atom has undergone ortho metalation to form a five-membered Ir(1)–Ir(2)–P(2)–C(401)–C(406) metallacycle. The $\mu_3\text{-}\kappa^2\text{-Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{P}(\eta^1\text{-o-C}_6\text{H}_4)$ ligand now acts as a six-electron donor, resulting in a “butterfly” geometry. The C_{60} ligand is coordinated to the lower “wing” of the “butterfly” composed of the Ir(1)–Ir(2)–Ir(3) triangle in a typical $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$ arene-type fashion, which has recently been reviewed.^{2a} All bond lengths and angles for **2** and **3**, including those for the carbonyl and C_{60} ligands, are within the expected ranges.

Concluding Remarks

In the transformation **1** $\rightarrow$ **2** $\rightarrow$ **3**, two PPh_3 ligands are converted to the diphosphine $\kappa^2\text{-Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{PPh}_2$ (for **2**) and in turn to $\mu_3\text{-}\kappa^2\text{-Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{P}(\eta^1\text{-o-C}_6\text{H}_4)$ (for **3**) on the Ir_4 cluster framework by successive ortho phosphorylation and ortho metalation processes. The “butterfly” structure of **3** is apparently stabilized by the multifunctional C_{60} ligand. A crossover experiment implies that the conversion **1** $\rightarrow$ **2** is an intramolecular reaction. Thus, plausible reaction pathways for the formation of **2** and **3** have been proposed. We are currently investigating facile synthetic methods for multifunctional phosphines from this re-

markable coupling reaction of phosphines on Ir_4 carbonyl clusters.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried over the appropriate drying agents and distilled immediately before use. C_{60} (99.5%, SES Research), $\text{Ir}_4(\text{CO})_{12}$ (98%, Strem), PPh_3 (99%, Aldrich), and KOH (85%, Junsei) were used without further purification. $\text{Ir}_4(\text{CO})_{10}\text{(PPh}_3)_2$ was prepared according to the literature method.¹² Preparative thin-layer chromatography (TLC) plates were produced with GF254 silica gel (type 60, E. Merck). Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ^1H NMR (400 MHz) spectra were recorded on a Bruker AVANCE-400 spectrometer, and ^{31}P NMR (122 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Positive ion FAB mass spectra (FAB^+) was obtained by the staff of the Korea Basic Science Center, and the m/z value was referenced to ^{193}Ir . Elemental analyses were provided by the staff of the Energy and Environment Research Center at KAIST.

Preparation of $\text{Ir}_4(\text{CO})_7(\mu\text{-CO})_3\{\kappa^2\text{-Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{PPh}_2\}$ (2**).** A chlorobenzene solution (30 mL) of $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$ (**1**; 30 mg, 0.019 mmol) was heated at reflux for 10 min. Evaporation of the solvent and purification by preparative TLC ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1/1) gave **2** (15.1 mg, 0.010 mmol, 53%, $R_f = 0.7$) as an orange solid: IR (C_6H_{12}) $\nu(\text{CO})$ 2071 (m), 2040 (s), 2002 (m), 1992 (w), 1981 (w), 1855 (w), 1799 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 7.56 (m, 2H), 7.51 (m, 2H), 7.35–7.24 (m, 20H) (all $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$); $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CDCl_3 , 298 K) δ 23.2 (s); MS (FAB^+) m/z 1496 [M^+]. Anal. Calcd for $\text{C}_{40}\text{H}_{24}\text{Ir}_4\text{O}_{10}\text{P}_2$: C, 32.13; H, 1.62. Found: C, 31.95; H, 1.50.

Preparation of $\text{Ir}_4(\text{CO})_6(\mu\text{-CO})\{\mu_3\text{-}\kappa^2\text{-Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{P}(\eta^1\text{-o-C}_6\text{H}_4)\}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60})$ (3**).** A chlorobenzene solution (30 mL) of **1** (30 mg, 0.019 mmol) and C_{60} (2 equiv, 27 mg, 0.038 mmol) was heated at reflux for 2 h. Evaporation of the solvent and purification by preparative TLC ($\text{CS}_2/\text{CH}_2\text{Cl}_2$, 8/1) afforded compound **3** (20.3 mg, 0.010 mmol, 52%, $R_f = 0.6$) as a black solid: IR (CH_2Cl_2) $\nu(\text{CO})$ 2053 (vs), 2019 (vs), 2002 (vs), 1979 (sh), 1827 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.89 (m, phenyl, 1H), 8.09 (m, phenyl, 2H), 7.69–7.36 (m, phenyl, 15H); ^{31}P NMR (122 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, 298 K) δ 182.2 (s, 1P), 25.1 (s, 1P). Anal. Calcd for $\text{C}_{91}\text{H}_{18}\text{Ir}_4\text{O}_7\text{P}_2$: C, 53.21; H, 0.88. Found: C, 53.04; H, 0.83.

Reaction of **2 with C_{60} .** A chlorobenzene solution (30 mL) of **2** (30 mg, 0.020 mmol) and C_{60} (2.1 equiv, 30 mg, 0.042 mmol) was heated at reflux for 1.5 h. Evaporation of the solvent and purification by preparative TLC ($\text{CS}_2/\text{CH}_2\text{Cl}_2$, 8/1) produced compound **3** (29.2 mg, 0.014 mmol, 71%, $R_f = 0.6$) as a black solid.

Crystal Structure Determination. Crystals of **2** and **3** suitable for X-ray diffraction studies were obtained by an interlayer diffusion technique (methanol into a CH_2Cl_2 solution of **2**; heptane into a CS_2 solution of **3**). Diffraction data were collected on a Siemens SMART diffractometer/CCD area detector. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. Each series consisted of 15 frames collected at scan intervals of 0.3° in ω with an exposure time of 10 s per frame. A total of 12 533 (at 293 K) and 34 548 (at 293 K) data were collected for **2** and **3**, respectively. Total reflections were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Each structure was solved by direct¹³ and difference Fourier methods and was

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refined by full-matrix least-squares methods based on F^2 (SHELX 97).¹⁴ All non-hydrogen atoms were refined with anisotropic thermal coefficients. Details of relevant crystallographic data are summarized in Table 1.

Acknowledgment. This work was supported by the National Research Laboratory (NRL) Program of the

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Ministry of Science & Technology of Korea (MOST) and the Korea Science & Engineering Foundation (Project No. 1999-1-122-001-5).

Supporting Information Available: Figures and tables giving full crystallographic and structural data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM049303I