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# Ortho Phosphorylation of $PPh_3$ To Give a Diphosphine and Formation of a “Butterfly” Structure on a Tetrairidium Framework

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A brief thermolysis of the bis-phosphine-substituted tetrairidium cluster $Ir_4(CO)_{10}(PPh_3)_2$ (**1**) in chlorobenzene (CB) converts it rapidly to the diphosphine cluster $Ir_4(CO)_7(\mu\text{-}CO)_3\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2\}$ (**2**) in 53% yield, providing evidence for ortho phosphorylation at the tetrairidium cluster framework. Treatment of **2** with excess $C_{60}$ affords the “butterfly” $Ir_4{-}C_{60}$ complex $Ir_4(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**3**) in 71% yield. Interestingly, compound **3** can be prepared directly from the thermolysis of **1** with excess $C_{60}$ 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 $\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2$ ligand chelating one of the basal iridium atoms. In contrast, complex **3** possesses a “butterfly” geometry in which the $C_{60}$ ligand is coordinated to the lower wing of the “butterfly” by an arene type $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ 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 $C_{60}$ with metal clusters has been a topic of great interest in exohedral metallofullerene chemistry,[2] because $C_{60}$−metal cluster complexes have a direct analogy to carbon nanotubes functionalized with metal nanoparticles.[3] Furthermore, $C_{60}$−metal cluster complexes exhibit very strong electronic communication between $C_{60}$ 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 $C_{60}$−metal cluster complexes, since $C_{60}$ acts as an electron-withdrawing ligand. In our previous work, we examined the reactions of $C_{60}$ with phosphine-substituted metal clusters such as $Ir_4(CO)_9(PPh_3)_3$,[4] $Ir_4(CO)_8(PMe_3)_4$,[5] and $Rh_6(CO)_{12}(dppm)_2$.[6] As an extension of our studies on the chemistry of $C_{60}$−metal cluster complexes, we examined the reaction between $Ir_4(CO)_{10}(PPh_3)_2$ (**1**) and $C_{60}$. Herein we report the full details of synthesis and characterization of $Ir_4(CO)_7(\mu\text{-}CO)_3\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)\text{-}PPh_2\}$ (**2**) formed by ortho phosphorylation of $PPh_3$ and $Ir_4(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**3**) by stabilization of the “butterfly” structure from the reaction of tetrahedral **1** with $C_{60}$, as shown in Scheme 1.

## Results and Discussion

**Synthesis and Characterization of 2 and 3.** Thermolysis of $Ir_4(CO)_{10}(PPh_3)_2$ (**1**) in chlorobenzene (CB) at

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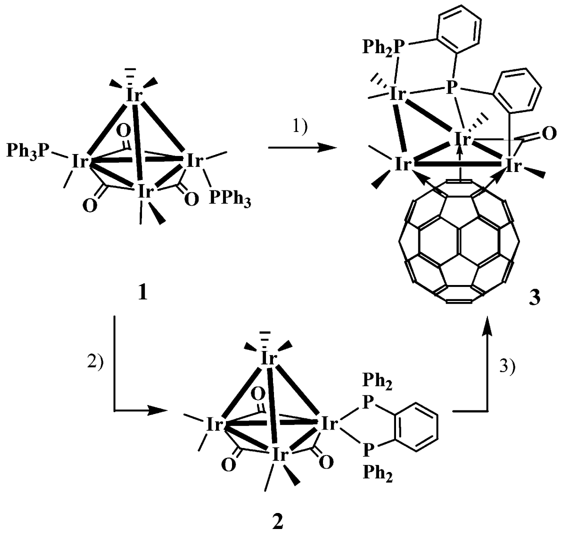
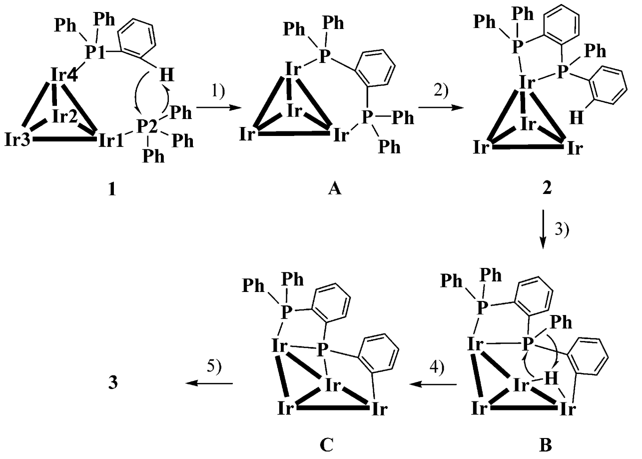
**Scheme 1**[a]



[a] Legend: (1) 2 equiv of $C_{60}$, $C_6H_5Cl$, 132 °C, 2 h; (2) $C_6H_5Cl$, 132 °C, 10 min; (3) 2 equiv of $C_{60}$, $C_6H_5Cl$, 132 °C, 2 h. Terminal carbonyl ligands have been omitted for clarity.

**Scheme 2**[a]



[a] Legend: (1) ortho phosphorylation, $-C_6H_6$; (2) rearrangement of the diphosphine ligand; (3) ortho metalation; (4) $-C_6H_6$; (5) $-3$ CO, $+C_{60}$. Carbonyl and $C_{60}$ 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, $Ir_4(CO)_7(\mu\text{-}CO)_3\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2\}$ (**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 $Ir_4-C_{60}$ derivative $Ir_4(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**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 $\delta$ 7.56, 7.51, and 7.35−7.24 assigned to aromatic protons. The signals at $\delta$ 7.56 and 7.51 correspond to four *o*-phenylene group protons, and the signals at $\delta$ 7.35−7.24 are assigned to the phenyl group protons. Similar chemical shifts for the four protons of the *o*-phenylene bridge (ca. $\delta$ 7.58) are observed in $Pd\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2\}Br_2$ (**4**).[7] The $^1H$ NMR spectrum of **3** shows multiplets in the aromatic region at $\delta$ 7.69−7.36 assigned to phenyl group protons. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at $\delta$ 23.2 for the two magnetically equivalent phosphorus atoms of the diphosphine ligand (cf. $\delta$ 64.2 in **4**).[7] The $^{31}P\{^1H\}$ NMR spectrum of **3** contains two singlets at $\delta$ 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 ($\delta$ 130−300).[4] The singlet at $\delta$ 25.1 is consistent with a terminal phosphorus atom bonded to an iridium center ($\delta$ −30 to +70).[4] Unfortunately, the mass spectrum of **3** could not be obtained.

A crossover experiment was carried out employing $Ir_4(CO)_{10}(PPh_3)_2$ (**1**) and $Ir_4(CO)_{10}(P(p\text{-}tol)_3)_2$ (*p*-tol = *p*-$C_6H_4CH_3$) in a 1:1 ratio, but crossover products, $Ir_4(CO)_7(\mu\text{-}CO)_3(PPh_3)_2\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(p\text{-}tol)_2\}$ and $Ir_4(CO)_7(\mu\text{-}CO)_3(PPh_3)_2\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_3CH_3)P(p\text{-}tol)_2\}$, were not detected. This observation suggests that the transformation **1** → **2** is intramolecular. From this mechanistic data, plausible reaction pathways for the conversion **1** → **2** → **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 $\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2$. 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 precedented in $Ir_4(CO)_{10}$(1,2-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 $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ coordination to one wing of the "butterfly".

In the transformation **1** → **2** → **3**, two $PPh_3$ ligands are converted to the diphosphine $\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2$ and further to a $\mu_3\text{-}\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)$ unit on the $Ir_4$ framework by successive ortho phosphorylation and ortho metalation, as illustrated in Scheme 2. Synthesis of phosphine ligands with $P-(C)_n-P$ and $P-(C)_n-P-(C)_n-P$ 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 | $3\cdot CS_2$ |
|---|---|---|
| formula | $C_{40}H_{24}Ir_4O_{10}P_2$ | $C_{91}H_{18}Ir_4O_7P_2\cdot CS_2$ |
| 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 |
| $\beta$, deg | 85.648(2) | 107.518(4) |
| $\gamma$ , 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) |
| $\lambda$(Mo Kα), Å | 0.71073 | 0.71073 |
| $\mu$, mm$^{-1}$ | 13.267 | 8.232 |
| $\theta_{min}$, $\theta_{max}$, 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) | | |

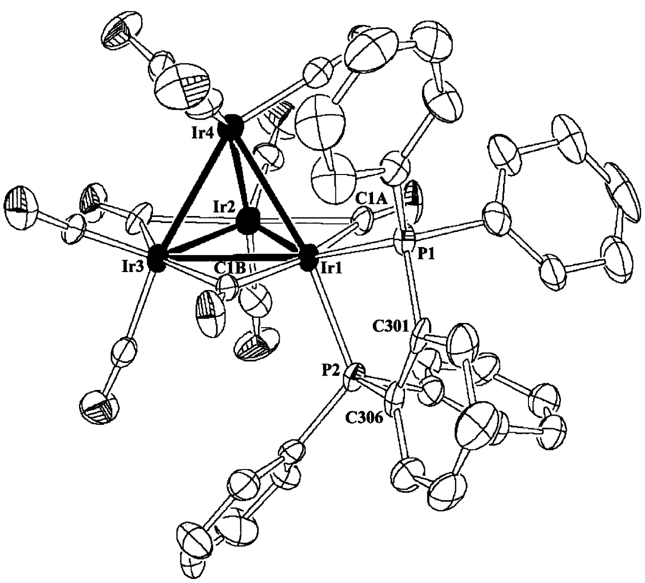

**Figure 1.** Molecular structure of **2**.

**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) |

thesis.[9] Instances of phosphine coupling to form a diphosphine on a metallic framework are rare, with two examples for Pd[7] and Ir[4] 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 $\kappa^2$-P($o$-$C_6H_4$)P ligand, a four-electron donor. The P(1) 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 $Ir_4(CO)_{10}$(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 $\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$-$C_{60}$ 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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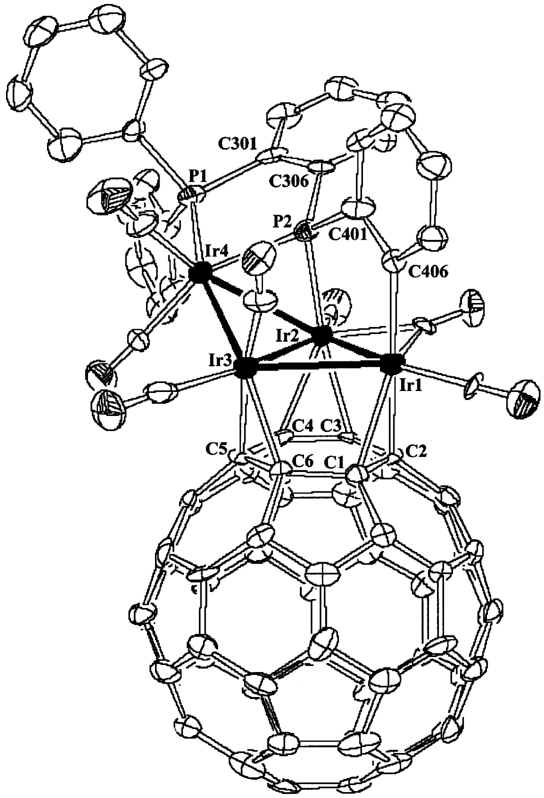

**Figure 2.** Molecular structure of **3**.

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 $\mu_3$-$\kappa^2$-$Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)$ 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 $\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$-$C_{60}$ 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** → **2** → **3**, two $PPh_3$ ligands are converted to the diphosphine $\kappa^2$-$Ph_2P(o\text{-}C_6H_4)PPh_2$ (for **2**) and in turn to $\mu_3$-$\kappa^2$-$Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)$ (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** → **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 remarkable 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), $Ir_4(CO)_{12}$ (98%, Strem), $PPh_3$ (99%, Aldrich), and KOH (85%, Junsei) were used without further purification. $Ir_4(CO)_{10}(PPh_3)_2$ 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 $Ir_4(CO)_7(\mu\text{-}CO)_3\{\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)PPh_2\}$ (2).** A chlorobenzene solution (30 mL) of $Ir_4(CO)_{10}(PPh_3)_2$ (**1**; 30 mg, 0.019 mmol) was heated at reflux for 10 min. Evaporation of the solvent and purification by preparative TLC ($CH_2Cl_2/C_6H_{14}$, 1/1) gave **2** (15.1 mg, 0.010 mmol, 53%, $R_f = 0.7$) as an orange solid: IR ($C_6H_{12}$) $\nu$(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) $\delta$ 7.56 (m, 2H), 7.51 (m, 2H), 7.35−7.24 (m, 20H) (all $C_6H_5$ + $C_6H_4$); $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 298 K) $\delta$ 23.2 (s); MS (FAB$^+$) *m/z* 1496 [M$^+$]. Anal. Calcd for $C_{40}H_{24}Ir_4O_{10}P_2$: C, 32.13; H, 1.62. Found: C, 31.95; H, 1.50.

**Preparation of $Ir_4(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}\kappa^2\text{-}Ph_2P(o\text{-}C_6H_4)P(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (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 ($CS_2/CH_2Cl_2$, 8/1) afforded compound **3** (20.3 mg, 0.010 mmol, 52%, $R_f = 0.6$) as a black solid: IR ($CH_2Cl_2$) $\nu$(CO) 2053 (vs), 2019 (vs), 2002 (vs), 1979 (sh), 1827 (w) cm$^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 298 K) $\delta$ 8.89 (m, phenyl, 1H), 8.09 (m, phenyl, 2H), 7.69−7.36 (m, phenyl, 15H); $^{31}P$ NMR (122 MHz, $C_6D_4Cl_2$, 298 K) $\delta$ 182.2 (s, 1P), 25.1 (s, 1P). Anal. Calcd for $C_{91}H_{18}Ir_4O_7P_2$: 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 ($CS_2/CH_2Cl_2$, 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 $\omega$ scans at different starting angles. Each series consisted of 15 frames collected at scan intervals of 0.3° in $\omega$ 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 direct[13] 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.

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**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.

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