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## Two Metal Centers Bridging Two C<sub>60</sub> Cages as a Wide Passage for Efficient Interfullerene Electronic Interaction

Gaehang Lee,<sup>†</sup> Youn-Jaung Cho,<sup>†</sup> Bo Keun Park,<sup>†</sup> Kwangyeol Lee,<sup>\*,‡</sup> and Joon T. Park<sup>\*,†</sup>

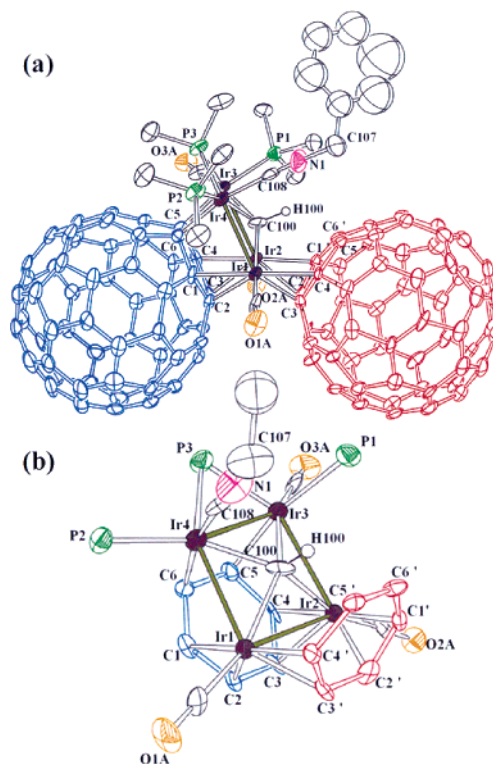
National Research Laboratory, Department of Chemistry and School of Molecular Science (BK 21),  
Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701, Korea, and  
Department of Chemistry, Korea University, Seoul, 136-701, Korea

Received July 7, 2003; E-mail: joontpark@kaist.ac.kr; kylee1@korea.ac.kr

Exohedral metallofullerenes have attracted a lot of attention concerning the effects of metal coordination on the chemical and physical properties of C<sub>60</sub>.<sup>1</sup> In particular, the investigation on the C<sub>60</sub>–metal cluster chemistry has unraveled an aspect of C<sub>60</sub> as a versatile, multifunctional ligand exhibiting various  $\sigma$ - and  $\pi$ -type bonding modes.<sup>2,3</sup> C<sub>60</sub>–metal cluster complexes have a direct analogy to carbon nanotubes decorated by metal nanoparticles<sup>4</sup> and exhibit very strong electronic communication between C<sub>60</sub> and metal cluster centers that can be fine-tuned with ligands attached on the metal centers.<sup>2,3c</sup> Furthermore, the electrochemical studies of robust self-assembled monolayers (SAMs) based on C<sub>60</sub>–cluster compounds reveal that the solution electrochemical behavior of C<sub>60</sub> is directly transferred to a two-dimensional surface structure.<sup>5</sup> Our efforts in this field culminate in the recent preparation of the first bisfullerene complex with a Rh<sub>6</sub> cluster bridge,<sup>6</sup> which serves as a direct model for two carbon nanotubes connected by a heterogeneous inorganic junction. This compound shows unusually strong electronic communication between two C<sub>60</sub> cages via one metal atom bridge.<sup>6</sup> Prior to our study, only weak interfullerene electronic communications have been reported in organic-based bisfullerene compounds, which are of considerable interest due to their potential for future optical and electronic applications.<sup>7</sup> Herein, we report the preparation of a new C<sub>60</sub>–Ir<sub>4</sub> metal sandwich complex with a novel  $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$  bonding mode and further enhancement of the interfullerene electronic communication by inserting two metal atoms as a bridge between two C<sub>60</sub> cages, which act as a wide channel for efficient electronic communication.

Reaction of Ir<sub>4</sub>(CO)<sub>8</sub>(PMe<sub>3</sub>)<sub>4</sub><sup>8</sup> with 4 equiv of C<sub>60</sub> in refluxing 1,2-dichlorobenzene (DCB) for 2 h,<sup>9</sup> followed by treatment with 0.15 equiv of CNR (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) at 70 °C for 2 h, afforded a new green solid **1** as the major product (8%).<sup>10</sup> Compound **1** was formulated as Ir<sub>4</sub>(CO)<sub>5</sub>( $\mu_4\text{-CH}$ )(PMe<sub>3</sub>)<sub>2</sub>( $\mu\text{-PMe}_2$ )(CNR)( $\mu\text{-}\eta^2, \eta^2\text{-C}_{60}$ )-( $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$ ) on the basis of microanalytical and NMR spectroscopic data as well as the following X-ray crystallographic study.

The molecular structure of **1** is shown in Figure 1.<sup>11</sup> Extensive structural changes have occurred for the Ir<sub>4</sub> metal framework and ligand coordination environments. The Ir<sub>4</sub> metal framework in **1** has a square-planar geometry, while the starting material Ir<sub>4</sub>(CO)<sub>8</sub>(PMe<sub>3</sub>)<sub>4</sub> adopts a tetrahedral core.<sup>8</sup> The overall valence electron count is 64e for **1** as expected for a metal cluster compound with a square-planar geometry. The Ir<sub>4</sub> framework is face-capped, surprisingly, by a methyne unit. The two metal atoms (Ir3 and Ir4), each coordinated with a terminal PMe<sub>3</sub> ligand, are bridged by a PMe<sub>2</sub> moiety. Interesting structural features are observed for the C<sub>60</sub>–metal interactions; two adjacent metals, Ir1 and Ir2, bridge the two C<sub>60</sub> units via a  $\mu\text{-}\eta^2, \eta^2\text{-C}_{60}$  bonding mode. The inner carbon atoms, C(2, 3) and C(2', 3'), of the butadiene-like moieties of the

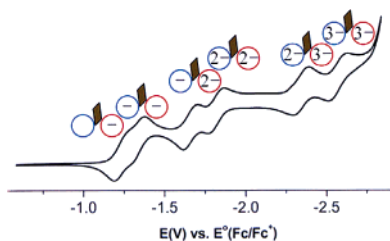


**Figure 1.** (a) Molecular geometry and atomic-labeling scheme for **1**. (b) Expanded view of ligated C<sub>6</sub> rings of the two C<sub>60</sub> ligands.

two C<sub>60</sub> units exhibit stronger interactions with metal atoms than the outer carbon atoms, C(1, 4) and C(1', 4'), as was previously observed for Os<sub>5</sub>C(CO)<sub>12</sub>(PPh<sub>3</sub>)( $\mu\text{-}\eta^2, \eta^2\text{-C}_{60}$ ).<sup>12</sup> Ir1–C2 = 2.16(1) Å; Ir2–C3 = 2.17(1) Å; Ir2–C2' = 2.14(1) Å; Ir1–C3' = 2.11(1) Å; Ir1–C1 = 2.20(1) Å; Ir2–C4 = 2.19(1) Å; Ir2–C1' = 2.19(1) Å; Ir1–C4' = 2.20(1) Å. The other two metal atoms, Ir3 and Ir4, bind to two carbon atoms (C5 and C6) of one C<sub>60</sub> unit in a  $\sigma$ -fashion, which is the first example of a novel  $\sigma$ – $\pi$  mixed type  $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$  bonding mode. The  $\sigma$ -interactions (Ir3–C5 = 2.17(1) Å and Ir4–C6 = 2.19(1) Å) are comparable to the  $\pi$ -type interactions unlike other known  $\sigma$ – $\pi$  mixed complexes, in which shorter bond distances are commonly observed for  $\sigma$ -bonds.<sup>13</sup> The cyclohexatriene-like C<sub>6</sub> ring in the  $\mu\text{-}\eta^2, \eta^2\text{-C}_{60}$  ligand shows alternation in C–C bond distances (av. 1.43 and 1.51 Å, respectively). However, the other C<sub>6</sub> ring in the  $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$  ligand exhibits the 1,3-cyclohexadiene-like nature; the bond lengths, C1–C2 (1.44(2) Å) and C3–C4 (1.49(2) Å), are shorter than the other four C–C bonds (av. 1.52 Å). The sums of three angles around sp<sup>3</sup>-hybridized C5 (334°) and C6 (333°) are considerably smaller than those of the other four carbon atoms (av. 347°) with sp<sup>2</sup> hybridization.<sup>14</sup> Similar protrusion of sp<sup>3</sup>-hybridized carbons

<sup>†</sup> Korea Advanced Institute of Science and Technology.

<sup>‡</sup> Korea University.



**Figure 2.** Cyclic voltammogram of **1** in chlorobenzene with  $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$  as the electrolyte (scan rate = 10 mV/s).

from the smooth curvature of the  $\text{C}_{60}$  ligand has been previously observed for related  $\sigma$ - $\pi$  mixed type  $\text{C}_{60}$ -cluster complexes.<sup>13</sup>

To address the origin of the face-capping  $\mu_4$ -CH unit, reaction of  $\text{Ir}_4(\text{CO})_8(\text{P}(\text{CD}_3)_3)_4$  with  $\text{C}_{60}$ , followed by treatment with benzyl isocyanide, was carried out. The  $\mu_4$ -CH signal at  $\delta$  15.52 is absent in the  $^1\text{H}$  NMR spectrum of the formed deuterium-labeled phosphine analogue of **1**, implying that a methyl group in a  $\text{PMe}_3$  ligand is the source of the resultant methyne moiety by P-C and C-H bond activation. Because three phosphorus atoms remain in **1**, reaction of stoichiometrically precise  $\text{Ir}_4(\text{CO})_9(\text{PMe}_3)_3$  with  $\text{C}_{60}$  was attempted only to result in severe decompositions. Additional  $\text{PMe}_3$  ligand in the starting material  $\text{Ir}_4(\text{CO})_8(\text{PMe}_3)_4$ , apparently, plays a crucial role in the formation of **1**.

The cyclic voltammogram (CV) of **1** exhibits six well-separated reversible, one-electron redox waves at  $-1.25$ ,  $-1.32$ ,  $-1.66$ ,  $-1.82$ ,  $-2.35$ ,  $-2.58$  V within the solvent cutoff window (Figure 2). Redox waves of **1** correspond to sequential, pairwise addition of six electrons into the two  $\text{C}_{60}$  moieties to form  $\text{C}_{60}^-\text{Ir}_4\text{C}_{60}^-$ ,  $\text{C}_{60}^{2-}\text{Ir}_4\text{C}_{60}^-$ ,  $\text{C}_{60}^{3-}\text{Ir}_4\text{C}_{60}^{2-}$ , ... and ultimately  $\text{C}_{60}^{3-}\text{Ir}_4\text{C}_{60}^{3-}$  (see Figure 2). The first redox wave in each pair in the CV is ascribed to that of  $\mu\text{-}\eta^1, \eta^2\text{-C}_{60}$  ligand, because the other  $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$  ligand bonded to phosphine coordinated metal atoms would experience a higher degree of metal-to- $\text{C}_{60}$   $\pi$ -back-donation. Overall, the redox waves of **1** are shifted to more negative potentials relative to those ( $-1.19$ ,  $-1.38$ ,  $-1.62$ ,  $-1.86$ ,  $-2.12$ , and  $-2.41$  V) of the related bisfullerene complex  $\text{Rh}_6(\text{CO})_5\text{-(dppm)}_2(\text{CNR})(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})_2$  (**2**) due to the stronger metal-to- $\text{C}_{60}$   $\pi$ -back-bonding in **1**. The second redox wave in each pair in the CV of **1** becomes increasingly separated from the first wave ( $\Delta(E_{1/2}^1, E_{1/2}^2) = 0.07$  V,  $\Delta(E_{1/2}^3, E_{1/2}^4) = 0.16$  V,  $\Delta(E_{1/2}^5, E_{1/2}^6) = 0.23$  V) as the reduction proceeds. Similar behavior was observed for **2** ( $\Delta(E_{1/2}^1, E_{1/2}^2) = 0.19$  V,  $\Delta(E_{1/2}^3, E_{1/2}^4) = 0.24$  V,  $\Delta(E_{1/2}^5, E_{1/2}^6) = 0.29$  V), which was proposed to stem from the effect of increasing Coulombic repulsion between the two  $\text{C}_{60}$  moieties.<sup>6</sup> Importantly, the increase in the separation within the redox pairs in **1** is abrupt ( $\Delta(E_{1/2}^3, E_{1/2}^4) - \Delta(E_{1/2}^1, E_{1/2}^2) = 0.09$  V;  $\Delta(E_{1/2}^5, E_{1/2}^6) - \Delta(E_{1/2}^3, E_{1/2}^4) = 0.07$  V), while a rather smooth increase is observed for **2** ( $\Delta(E_{1/2}^3, E_{1/2}^4) - \Delta(E_{1/2}^1, E_{1/2}^2) = 0.05$  V;  $\Delta(E_{1/2}^5, E_{1/2}^6) - \Delta(E_{1/2}^3, E_{1/2}^4) = 0.05$  V).<sup>6</sup> The distance between the two  $\text{C}_{60}$  units in **1** ( $d(\text{C}2\text{--C}3') = 3.23$  Å;  $d(\text{C}3\text{--C}2') = 3.25$  Å) is shorter than that (ca. 3.56 Å) in **2**. The larger increase in the separation within the redox pairs of **1**, however, cannot be explained solely by the stronger Coulombic repulsion, because only a small increase in redox pair separation is observed for compounds, such as  $\text{C}_{120}\text{O}^{15}$  and  $\text{C}_{120}(\text{SiPh}_2)$ ,<sup>16</sup> with much shorter interfullerene distances of  $\sim 1.5$  Å ( $\text{C}_{120}\text{O}$ :  $\Delta(E_{1/2}^3, E_{1/2}^4) - \Delta(E_{1/2}^1, E_{1/2}^2) = 0.02$  V;  $\Delta(E_{1/2}^5, E_{1/2}^6) - \Delta(E_{1/2}^3, E_{1/2}^4) = 0.08$  V;  $\text{C}_{120}(\text{SiPh}_2)$ :  $\Delta(E_{1/2}^3, E_{1/2}^4) - \Delta(E_{1/2}^1, E_{1/2}^2) = -0.01$  V;  $\Delta(E_{1/2}^5, E_{1/2}^6) - \Delta(E_{1/2}^3, E_{1/2}^4) = 0.06$  V). Therefore, the two metal atoms between the two  $\text{C}_{60}$  units in **1**, apparently, facilitate enhanced interfullerene electronic interaction by providing a wide passage for electronic

communication as compared to **2** in which only one metal center interconnects two  $\text{C}_{60}$  cages.

In conclusion, we have prepared a  $\text{C}_{60}\text{--Ir}_4$  metal cluster sandwich complex **1** with two metal centers bridging two  $\text{C}_{60}$  units, which exhibits a novel  $\mu_4\text{-}\eta^1, \eta^1, \eta^2, \eta^2\text{-C}_{60}$  bonding mode and an unusual formation of a  $\mu_4\text{-CH}$  moiety. Such  $\text{C}_{60}$ -metal  $\sigma$  complexes might be utilized for selective functionalization of  $\text{C}_{60}$ . Compound **1** reveals an enhanced electronic communication through a wide channel of two metal centers for efficient electronic communication. A detailed mechanistic study for the formation of **1** and an investigation on its reactivity are currently under way. In addition, we are investigating the electrochemical properties of SAMs based on the fullerene-metal sandwich complexes (**1** and **2**) for practical applications of this unique family of  $\text{C}_{60}$ -metal sandwich complexes in electronic device fabrication.

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**Supporting Information Available:** Synthesis, characterization, and details of the crystallographic studies of **1** (PDF) as well as an X-ray crystallographic file for **1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Crystallographic data for **2**: monoclinic, space group  $P2_1/n$ ,  $a = 18.139(2)$  Å,  $b = 24.386(3)$  Å,  $c = 22.478(3)$  Å,  $\beta = 110.283(2)^\circ$ ,  $V = 9327(2)$  Å<sup>3</sup>,  $Z = 4$ ; crystal size  $0.45 \times 0.18 \times 0.08$  mm<sup>3</sup>. Diffraction data were collected at 173 K on a Bruker SMART diffractometer/CCD area detector. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give  $R = 0.0646$  and  $R_w = 0.1528$  (based on  $F^2$ ) for 1374 variables and 12 207 unique reflections with  $I > 2\sigma(I)$  and  $1.25 < \theta < 28.28$ .
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