

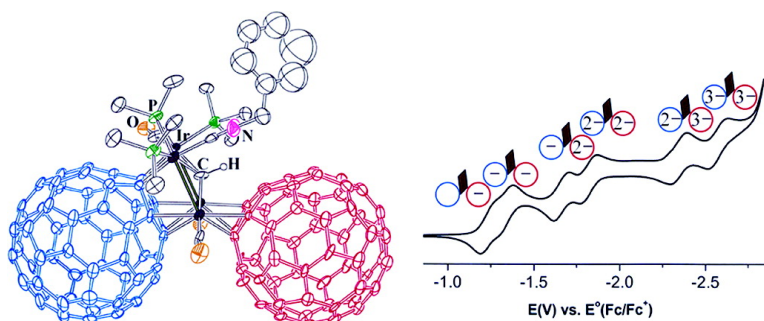
Communication

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Two Metal Centers Bridging Two C₆₀ Cages as a Wide Passage for Efficient Interfullerene Electronic Interaction

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Exohedral metallofullerenes have attracted a lot of attention concerning the effects of metal coordination on the chemical and physical properties of C₆₀.¹ In particular, the investigation on the C₆₀–metal cluster chemistry has unraveled an aspect of C₆₀ as a versatile, multifunctional ligand exhibiting various σ - and π -type bonding modes.^{2,3} C₆₀–metal cluster complexes have a direct analogy to carbon nanotubes decorated by metal nanoparticles⁴ and exhibit very strong electronic communication between C₆₀ and metal cluster centers that can be fine-tuned with ligands attached on the metal centers.^{2,3c} Furthermore, the electrochemical studies of robust self-assembled monolayers (SAMs) based on C₆₀–cluster compounds reveal that the solution electrochemical behavior of C₆₀ is directly transferred to a two-dimensional surface structure.⁵ Our efforts in this field culminate in the recent preparation of the first bisfullerene complex with a Rh₆ cluster bridge,⁶ 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 C₆₀ cages via one metal atom bridge.⁶ 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.⁷ Herein, we report the preparation of a new C₆₀–Ir₄ metal sandwich complex with a novel μ_4 - $\eta^1, \eta^1, \eta^2, \eta^2$ -C₆₀ bonding mode and further enhancement of the interfullerene electronic communication by inserting two metal atoms as a bridge between two C₆₀ cages, which act as a wide channel for efficient electronic communication.

Reaction of Ir₄(CO)₈(PMe₃)₄⁸ with 4 equiv of C₆₀ in refluxing 1,2-dichlorobenzene (DCB) for 2 h,⁹ followed by treatment with 0.15 equiv of CNR (R = CH₂C₆H₅) at 70 °C for 2 h, afforded a new green solid **1** as the major product (8%).¹⁰ Compound **1** was formulated as Ir₄(CO)₅(μ_4 -CH)(PMe₃)₂(μ -PMe₂)(CNR)(μ - η^2, η^2 -C₆₀)-(μ_4 - $\eta^1, \eta^1, \eta^2, \eta^2$ -C₆₀) 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 1.¹¹ Extensive structural changes have occurred for the Ir₄ metal framework and ligand coordination environments. The Ir₄ metal framework in **1** has a square-planar geometry, while the starting material Ir₄(CO)₈(PMe₃)₄ adopts a tetrahedral core.⁸ The overall valence electron count is 64e for **1** as expected for a metal cluster compound with a square-planar geometry. The Ir₄ framework is face-capped, surprisingly, by a methyne unit. The two metal atoms (Ir3 and Ir4), each coordinated with a terminal PMe₃ ligand, are bridged by a PMe₂ moiety. Interesting structural features are observed for the C₆₀–metal interactions; two adjacent metals, Ir1 and Ir2, bridge the two C₆₀ units via a μ - η^2, η^2 -C₆₀ bonding mode. The inner carbon atoms, C(2, 3) and C(2', 3'), of the butadiene-like moieties of the

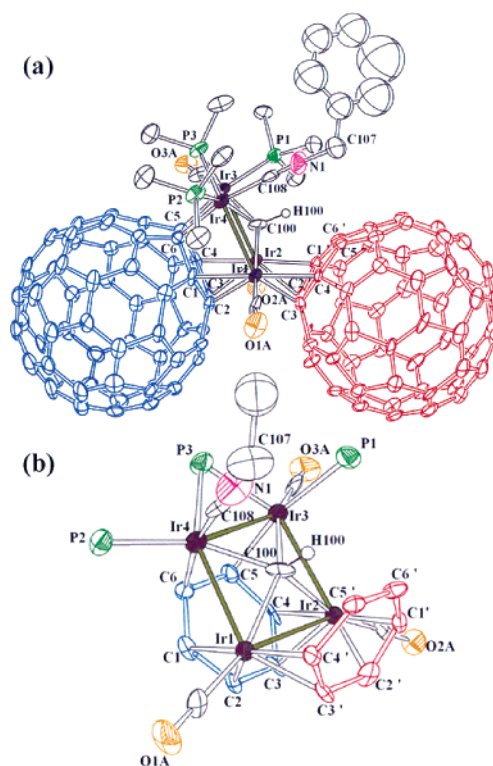


Figure 1. (a) Molecular geometry and atomic-labeling scheme for **1**. (b) Expanded view of ligated C₆ rings of the two C₆₀ ligands.

two C₆₀ units exhibit stronger interactions with metal atoms than the outer carbon atoms, C(1, 4) and C(1', 4'), as was previously observed for Os₅C(CO)₁₂(PPh₃)(μ - η^2, η^2 -C₆₀):¹² 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 C₆₀ unit in a σ -fashion, which is the first example of a novel σ - π mixed type μ_4 - $\eta^1, \eta^1, \eta^2, \eta^2$ -C₆₀ bonding mode. The σ -interactions (Ir3–C5 = 2.17(1) Å and Ir4–C6 = 2.19(1) Å) are comparable to the π -type interactions unlike other known σ - π mixed complexes, in which shorter bond distances are commonly observed for σ -bonds.¹³ The cyclohexatriene-like C₆ ring in the μ - η^2, η^2 -C₆₀ ligand shows alternation in C–C bond distances (av. 1.43 and 1.51 Å, respectively). However, the other C₆ ring in the μ_4 - $\eta^1, \eta^1, \eta^2, \eta^2$ -C₆₀ 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 sp³-hybridized C5 (334°) and C6 (333°) are considerably smaller than those of the other four carbon atoms (av. 347°) with sp² hybridization.¹⁴ Similar protrusion of sp³-hybridized carbons

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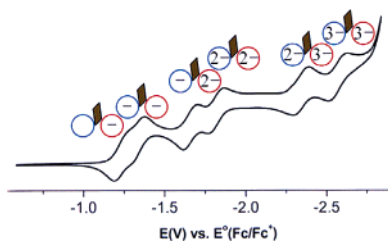


Figure 2. Cyclic voltammogram of **1** in chlorobenzene with $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$ as the electrolyte (scan rate = 10 mV/s).

from the smooth curvature of the C_{60} ligand has been previously observed for related $\sigma\text{-}\pi$ mixed type C_{60} -cluster complexes.¹³

To address the origin of the face-capping $\mu_4\text{-CH}$ unit, reaction of $\text{Ir}_4(\text{CO})_8(\text{P}(\text{CD}_3)_3)_4$ with C_{60} , followed by treatment with benzyl isocyanide, was carried out. The $\mu_4\text{-CH}$ signal at δ 15.52 is absent in the ^1H NMR spectrum of the formed deuterium-labeled phosphine analogue of **1**, implying that a methyl group in a 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 C_{60} was attempted only to result in severe decompositions. Additional 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 C_{60} moieties to form $\text{C}_{60}\text{-Ir}_4\text{-C}_{60}^-$, $\text{C}_{60}^-\text{-Ir}_4\text{-C}_{60}^-$, $\text{C}_{60}^-\text{-Ir}_4\text{-C}_{60}^{2-}$, ... 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- C_{60} π -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 $\text{Rh}_6(\text{CO})_5\text{-}(\text{dppm})_2(\text{CNR})(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})_2$ (**2**) due to the stronger metal-to- C_{60} π -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 C_{60} moieties.⁶ 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).⁶ The distance between the two 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 $\text{C}_{120}(\text{SiPh}_2)$,¹⁶ with much shorter interfullerene distances of ~ 1.5 Å (C_{120}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 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 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 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 C_{60} -metal σ complexes might be utilized for selective functionalization of 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 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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- (9) A new green compound identified by analytical TLC (silica gel) could not be further characterized because of its marginal solubility after solvent removal. To increase solubility, further derivatization by a benzyl isocyanide ligand was necessary.
- (10) IR (CS_2) ν_{CN} 2159 (w) cm^{-1} ; ν_{CO} 1986 (s) cm^{-1} ; ^1H NMR ($1,2\text{-C}_6\text{D}_4\text{Cl}_2$, 298 K) δ 15.52 (d, 1H, $J_{\text{PH}} = 13.0$ Hz, $\mu_4\text{-CH}$), 7.66–7.20 (m, 5H, $\text{CNCH}_2\text{C}_6\text{H}_5$), 5.18 (AB pattern, 2H, $J = 16.5$ Hz, $\text{CNCH}_2\text{C}_6\text{H}_5$), 3.55 (d, 3H, $J_{\text{PH}} = 7.0$ Hz, $\text{CH}_3\text{-}\mu\text{-P-CH}_3$), 3.04 (d, 3H, $J_{\text{PH}} = 4.6$ Hz, $\text{CH}_3\text{-}\mu\text{-P-CH}_3$), 2.07 (d, 9H, $J_{\text{PH}} = 9.8$ Hz, PMe_3), 1.86 (d, 9H, $J_{\text{PH}} = 9.1$ Hz, PMe_3); $^{31}\text{P}\{^1\text{H}\}$ NMR ($1,2\text{-C}_6\text{D}_4\text{Cl}_2$, 298 K) δ 164.3 (s, 1P, $\mu\text{-PMe}_3$), -44.9 (s, 1P, PMe_3), -47.9 (s, 1P, PMe_3). Anal. Calcd for $\text{C}_{147}\text{H}_{32}\text{O}_3\text{NP}_3\text{Ir}_4$: C, 63.75; H, 1.22; N, 0.53. Found: C, 63.40; H, 1.59; N, 0.81. Attempts to obtain mass spectroscopic data (FAB⁺, FAB⁻, and MALDI TOF) have not been successful.
- (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, $\beta = 110.283(2)^\circ$, $V = 9327(2)$ Å³, $Z = 4$; crystal size $0.45 \times 0.18 \times 0.08$ mm³. 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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- (14) $\angle\text{C}4\text{-C}5\text{-C}19 + \angle\text{C}4\text{-C}5\text{-C}6 + \angle\text{C}19\text{-C}5\text{-C}6 = 334^\circ$; $\angle\text{C}7\text{-C}6\text{-C}1 + \angle\text{C}7\text{-C}6\text{-C}5 + \angle\text{C}1\text{-C}6\text{-C}5 = 333^\circ$. See Supporting Information.
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