

# [60]Fullerene—Metal Cluster Complexes: Novel Bonding Modes and Electronic Communication

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## ABSTRACT

[60]Fullerene can bind a variety of metal clusters via  $\eta^2$ -C<sub>60</sub>,  $\mu$ - $\eta^2$ : $\eta^2$ -C<sub>60</sub>, and  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub>  $\pi$ -type bonding modes. Multiple C<sub>60</sub> additions to a single cluster core have also been demonstrated. Modification of the coordination sphere of cluster moieties has resulted in novel transformation of the coordination mode of the C<sub>60</sub> ligand between  $\pi$  and  $\sigma$  ( $\mu_3$ - $\eta^1$ : $\eta^1$ : $\eta^2$ -C<sub>60</sub> and  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$ -C<sub>60</sub>) types as well as reversible interconversion between  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub> and  $\mu$ - $\eta^2$ : $\eta^2$ -C<sub>60</sub>. The  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub> metal cluster complexes show remarkable electrochemical stability and an unusually strong electronic communication between C<sub>60</sub> and metal cluster centers.

## Introduction

Full-fledged research efforts in C<sub>60</sub> science, made possible by the availability of fullerene C<sub>60</sub> in mass quantity,<sup>1</sup> have produced numerous fullerene derivatives.<sup>2,3</sup> In particular, 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> as well as with the direct analogy to carbon nanotubes decorated by metal nanoparticles.<sup>3,4</sup> Prior to our investigations on the interaction between C<sub>60</sub> and metal clusters, exohedral

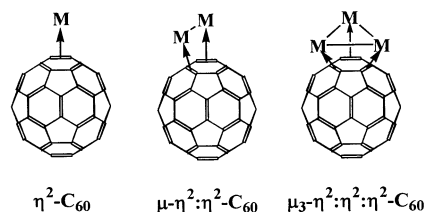
Kwangyeol Lee, born in 1971, received his B.S. degree from KAIST in 1992 and his Ph.D. degree, under the supervision of Prof. John R. Shapley, from University of Illinois at Urbana—Champaign in 1997. Since 1998, he has been working as a postdoctoral associate in Prof. Park's group at KAIST. His research interests are in metallofullerene chemistry, fullerene-based materials application, and nanostructured materials.

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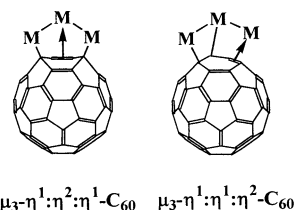
Joon T. Park, born in 1949, received his B.S. in chemistry at Seoul National University in 1972 and M.S. in physical chemistry at KAIST in 1975. He then spent four years at the chemistry division of the Agency for Defense Development (ADD). He came to the United States in 1979, completed his M.S. in organic chemistry in 1981, and obtained his Ph.D. degree in inorganic chemistry from University of Illinois at Urbana—Champaign, under the direction of John R. Shapley, in 1983. After postdoctoral work at duPont Central Research in Washington with Dr. Patricia A. Watson, he returned to ADD as a senior researcher in 1984. In 1986, he moved to KAIST as an Assistant Professor and was appointed as Professor of Chemistry in 1993. His research interests include C<sub>60</sub>—metal cluster complexes, group 4 metallocene-type catalysts for olefin polymerization, and single-source precursors for thin films and nanomaterials of group 13 nitrides and metal oxides.

metallofullerene chemistry was dominated by  $\pi$ -type C<sub>60</sub>—metal interactions with  $\eta^2$ -C<sub>60</sub> (for most metals)<sup>5</sup> and  $\mu$ - $\eta^2$ : $\eta^2$ -C<sub>60</sub> (for bimetallic Re<sub>2</sub>, Ru<sub>2</sub>, and Ir<sub>2</sub>)<sup>6</sup> bonding modes. Our group and that of Shapley have independently prepared various C<sub>60</sub>—metal cluster complexes and demonstrated that a variety of cluster frameworks [Re<sub>3</sub>( $\mu$ -H)<sub>3</sub>,<sup>7</sup> Ru<sub>3</sub>,<sup>8,9</sup> Os<sub>3</sub>,<sup>10–12</sup> Ru<sub>5</sub>C,<sup>13,14</sup> Os<sub>5</sub>C,<sup>15,16</sup> PtRu<sub>5</sub>C,<sup>14</sup> Ru<sub>6</sub>C,<sup>13</sup> and Rh<sub>6</sub><sup>17</sup>] can bind to C<sub>60</sub> via a face-capping cyclohexatriene-like bonding mode,  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub>. In particular, we have been interested in converting the  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub> bonding mode to new ones by modifying the coordination sphere of the metal centers to which C<sub>60</sub> is coordinated, and we have unraveled an aspect of C<sub>60</sub> as a versatile, multifunctional ligand exhibiting various  $\pi$ - and  $\sigma$ -bonding modes. We also demonstrated an unusually strong electronic communication between C<sub>60</sub> and metal cluster centers that can be readily fine-tuned with attached ligands on the metal cluster. Although there have been several reviews on metallofullerene complexes featuring our earlier results,<sup>3</sup> they fall short of describing the significant advances achieved recently in the area of C<sub>60</sub>—metal cluster complexes. In this Account, we aim to discuss general synthetic methods, novel bonding modes of the C<sub>60</sub> ligand on cluster frameworks, and unique electrochemical properties of C<sub>60</sub>—metal cluster complexes.

### $\pi$ complex



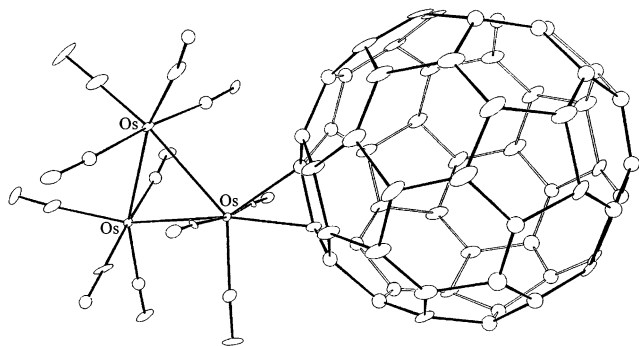
### $\sigma$ - $\pi$ mixed complex



## Synthesis and Structural Characterization of $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub> Metal Clusters

[60]Fullerene—metal cluster complexes have been prepared either by direct thermal reaction of the second-row transition metal carbonyl clusters with C<sub>60</sub> or by chemical activation of the third-row metal carbonyl clusters with Me<sub>3</sub>NO/MeCN followed by reaction with C<sub>60</sub>.<sup>7–17</sup> Chlorobenzene is the solvent of choice for the preparation of the C<sub>60</sub>—metal cluster complexes because it dissolves a large quantity of C<sub>60</sub>, has a relatively high boiling point that is useful for thermal reactions, and can be easily

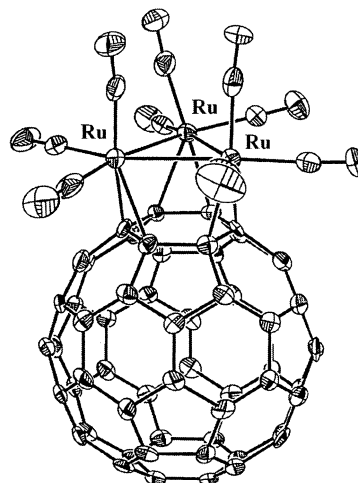
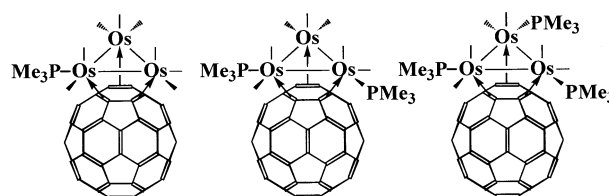
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FIGURE 1. Molecular structure of **1**.

removed under vacuum due to its high volatility. Most  $C_{60}$ –metal cluster compounds thus prepared are soluble in solvents such as carbon disulfide, toluene, chlorobenzene, and 1,2-dichlorobenzene.

**Trinuclear Clusters.** The first  $C_{60}$ –metal cluster complex,  $Os_3(CO)_{11}(\eta^2-C_{60})$  (**1**),<sup>18,19</sup> was prepared from the reaction of  $Os_3(CO)_{11}(NCMe)$  and  $C_{60}$ . The  $C_{60}$  moiety in **1** takes an equatorial position at an osmium atom in an  $\eta^2$  fashion by binding through a 6–6 ring fusion, as shown in Figure 1. The  $Os-C_2$  ( $C_{60}$ ) bond lengths (2.21 and 2.26 Å) are comparable to those in other  $\eta^2-C_{60}$  complexes.<sup>5</sup> The metal-coordinated C–C ( $C_{60}$ ) bond length of 1.42 Å is only slightly elongated from 1.38 Å, the length of an unperturbed double bond of  $C_{60}$ , implying that the  $\pi$ -backdonation in **1** is significantly suppressed by the presence of strong  $\pi$ -acid carbonyl ligands on the osmium atoms. Longer C–C distances have been observed for other  $\eta^2-C_{60}$  complexes with donor phosphine ligands at the metal center: 1.45 Å in  $Pd(PPh_3)_2(\eta^2-C_{60})$ ,<sup>5f</sup> 1.48 Å in  $RhH(CO)(PPh_3)_2(\eta^2-C_{60})$ ,<sup>5g</sup> 1.50 Å in  $W(CO)_3(dppe)(\eta^2-C_{60})$ ,<sup>5h</sup> and 1.53 Å in  $Ir(CO)Cl(PPh_3)_2C_{60}$ .<sup>5b</sup> Various substitution products of **1**, such as  $Os_3(CO)_{10}(NCMe)(\eta^2-C_{60})$ ,  $Os_3(CO)_{10}(PPh_3)(\eta^2-C_{60})$ , and  $Os_3(CO)_9(PR_3)_2(\eta^2-C_{60})$  ( $R = Me, Ph$ ), have also been prepared and characterized.<sup>10</sup>

Successive losses of the carbonyl ligands from **1** might be expected to form  $\mu-\eta^2-\eta^2-C_{60}$  and  $\mu_3-\eta^2-\eta^2-\eta^2-C_{60}$  complexes, but thermolysis of  $Os_3(CO)_{10}(NCMe)(\eta^2-C_{60})$  affords  $Os_3(CO)_9(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  (**2**) as the only product (23%).<sup>10</sup> A better yield (32%) was obtained from an alternative reaction of  $Os_3(CO)_{10}(NCMe)_2$  and  $C_{60}$  in refluxing chlorobenzene.<sup>10</sup> The first structural details of the  $\mu_3-\eta^2-\eta^2-\eta^2-C_{60}$  bonding mode were elucidated by Shapley et al. on the complex  $Ru_3(CO)_9(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  (**3**, see Figure 2), which is obtained from the reaction between  $Ru_3(CO)_{12}$  and  $C_{60}$  in refluxing hexane (4%) or chlorobenzene (16%).<sup>8</sup> The  $Ru_3$  triangle is positioned centrally over a six-membered carbon ring in  $C_{60}$ , and the two planes are essentially parallel (dihedral angle = 0.9°). The  $C_6$ -ring of  $C_{60}$  takes the form of cyclohexatriene, with each of its double bonds coordinated to a metal center. The average metal-coordinated C–C ( $C_{60}$ ) bond length (1.43 Å) and the average M–C ( $C_{60}$ ) length (2.27 Å) in **3** show little difference from those in **1**. The failure to form stable  $M(\eta^6-C_{60})$  compounds has been attributed to the curvature of  $C_{60}$ , which orients each exohedral p- $\pi$  orbital at an angle (ca. 10°) away from perpendicular to the face of the  $C_6$ -

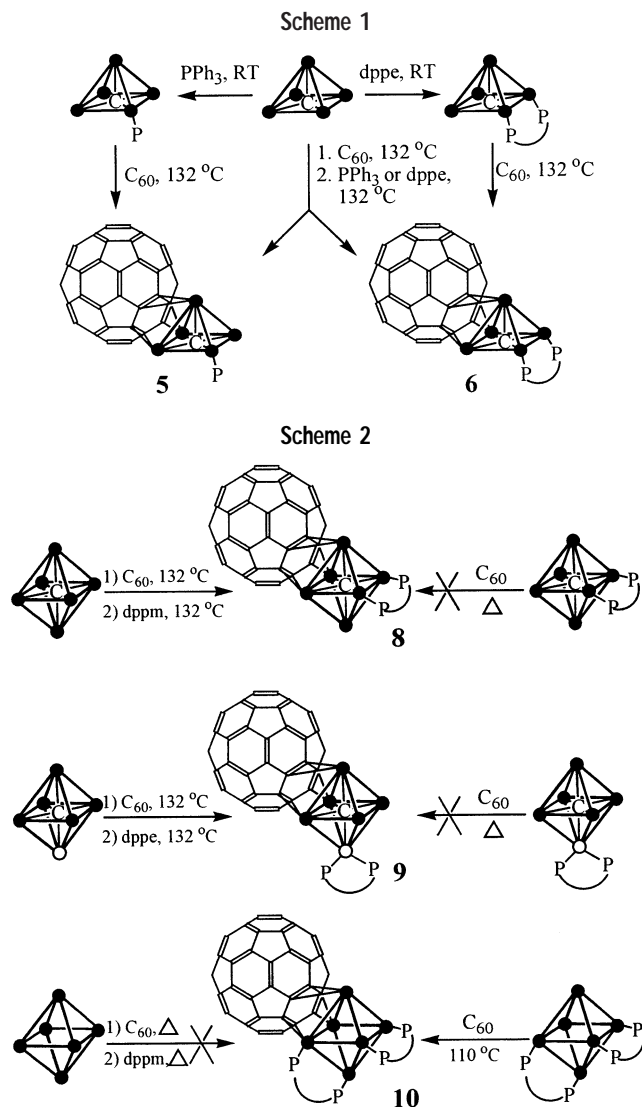
FIGURE 2. Molecular structure of **3**.FIGURE 3. Propeller-like geometry for phosphine substitution in **2**.

ring.<sup>20</sup> The geometry of the metal triangle in **3**, however, provides effective overlap with the  $C_{60}$  p- $\pi$  orbitals. A similar face-capping bonding pattern was previously reported for cluster compounds with benzene or related arenes.<sup>21</sup>

Homologous complexes **2** and **3** undergo carbonyl substitution reactions with phosphine ligands to afford  $M_3(CO)_{9-n}(PPh_3)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  ( $M = Ru, Os; n = 1, 2$ )<sup>9,11</sup> or  $M_3(CO)_{9-n}(PMe_3)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  ( $M = Os; n = 1, 2, 3$ )<sup>12</sup> by reaction of lightly stabilized  $Os_3(CO)_{9-n}(NCMe)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  with a corresponding phosphine and by thermal reaction of **3** with  $PPh_3$ , respectively. A propeller-like geometry is adopted for the phosphine ligands at the equatorial positions in  $Os_3(CO)_{9-n}(PMe_3)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  ( $n = 1, 2, 3$ ), as shown in Figure 3.<sup>12</sup>

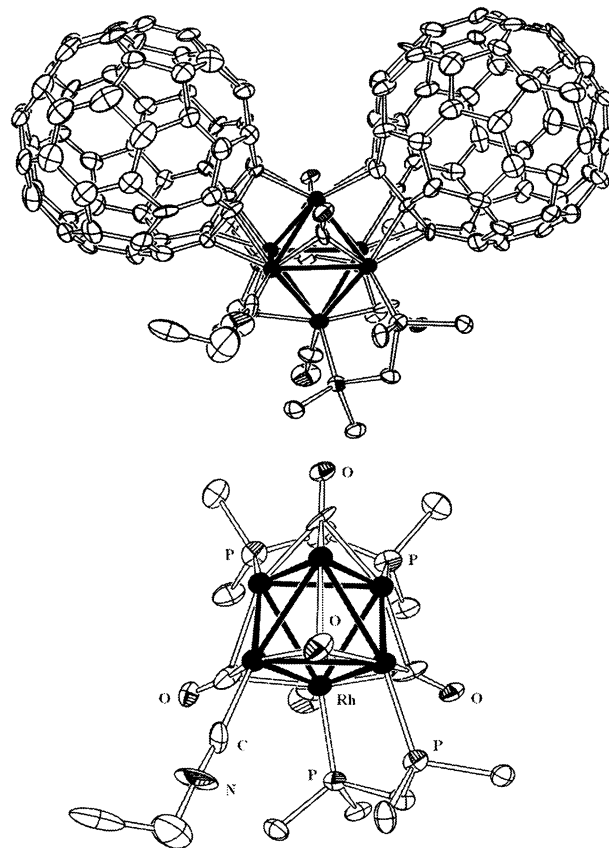
Another lightly stabilized third-row metal cluster,  $Re_3(\mu-H)_3(CO)_{11}(NCMe)$ , reacts with  $C_{60}$  to produce  $Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  (**4**) in 50% yield.<sup>7</sup> Compound **4** forms monosubstitution products  $Re_3(\mu-H)_3(CO)_8(L)(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  ( $L = PPh_3$  or  $CNCH_2Ph$ ) by chemical activation with  $Me_3NO/MeCN$  and subsequent reaction with  $PPh_3$  in refluxing chlorobenzene or by treatment with  $PhCH_2N=PPh_3$  at room temperature.<sup>7</sup> Interestingly, the phosphine or isocyanide ligand in these compounds takes an axial position on a rhenium atom for both steric and electronic reasons.<sup>7</sup>

**Penta- or Hexanuclear Clusters.** Reaction of a pentanuclear, square-pyramidal carbido cluster  $Ru_5C(CO)_{15}$  with  $C_{60}$  in refluxing chlorobenzene, followed by addition of  $PPh_3$  or 1,2-bis(dipheylphosphino)ethane ( $dppe$ ), forms  $Ru_5C(CO)_{11}(PPh_3)(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  (**5**) and  $Ru_5C(CO)_{10}(dppe)(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$  (**6**), respectively (Scheme 1).<sup>13,14</sup> Complexes **5** and **6** can be alternatively prepared by direct reaction



of phosphine-substituted  $\text{Ru}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$  or  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppe})$  with  $\text{C}_{60}$ . Regardless of the reaction sequence, the ligand substitution reactions are regiospecific. The  $\text{C}_{60}$  is coordinated to a triangular face of square-pyramidal  $\text{Ru}_5\text{C}$  framework, and the phosphine ligand coordinates the basal ruthenium atom that does not interact with the  $\text{C}_{60}$  ligand. The osmium analogue of **5**,  $\text{Os}_5\text{C}(\text{CO})_{11}(\text{PPh}_3)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_{60})$  (**7**) is obtained by chemical activation of  $\text{Os}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$  with 2 equiv of  $\text{Me}_3\text{NO}/\text{MeCN}$  at room temperature, followed by reaction with  $\text{C}_{60}$  in refluxing chlorobenzene.<sup>15,16</sup>

Three hexanuclear octahedral cluster frameworks,  $\text{Ru}_6\text{C}$ ,<sup>13</sup>  $\text{PtRu}_5\text{C}$ ,<sup>14</sup> and  $\text{Rh}_6$ ,<sup>17</sup> can interact with  $\text{C}_{60}$  via the  $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}$  bonding mode, as shown in Scheme 2. Reaction of  $\text{Ru}_6\text{C}(\text{CO})_{17}$  with  $\text{C}_{60}$  in refluxing chlorobenzene, followed by addition of 1,2-bis(diphenylphosphino)methane (dppm), produces  $\text{Ru}_6\text{C}(\text{CO})_{12}(\text{dppm})(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_{60})$  (**8**),<sup>13</sup> and a similar treatment of  $\text{PtRu}_5\text{C}(\text{CO})_{16}$  or  $\text{PtRu}_5\text{C}(\text{CO})_{14}(\text{COD})$  with  $\text{C}_{60}$  and dppe forms  $\text{PtRu}_5\text{C}(\text{CO})_{11}(\text{dppe})(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_{60})$  (**9**).<sup>14</sup> The non-carbido hexanuclear complex  $\text{Rh}_6(\text{CO})_9(\text{dppm})_2(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_{60})$  (**10**) can be prepared by direct thermal interaction of  $\text{Rh}_6(\text{CO})_{12}(\text{dppm})_2$  with  $\text{C}_{60}$ .<sup>17</sup> Interestingly, syntheses of hexanuclear  $\text{C}_{60}$  cluster com-

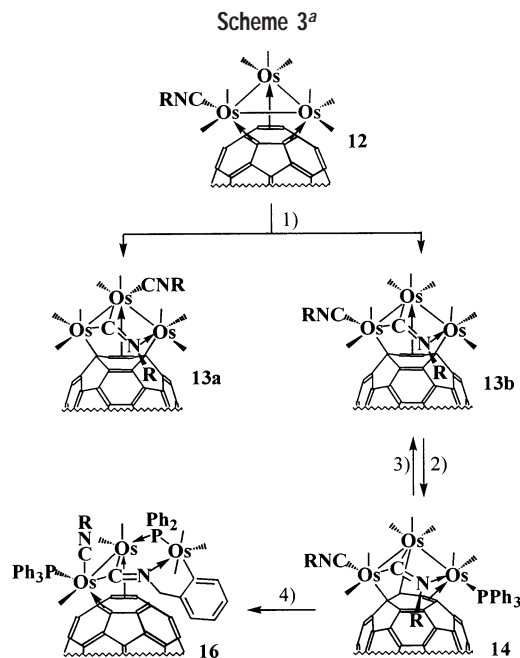


**FIGURE 4.** Molecular structure of **11**. Phenyl groups except ipso-carbons are removed for clarity.

plexes are specific to the preparation methods, as shown in Scheme 2.

**Multiple  $\text{C}_{60}$  Coordination on a Single Cluster Core.** Until recently, multiple coordination of  $\text{C}_{60}$  to a single metal center had not been accomplished, even though  $\text{C}_{60}$ , with a cone angle of  $120^\circ$ , is not an exceptionally bulky ligand. However, a metal cluster such as  $\text{Rh}_6(\text{CO})_{12}(\text{dppm})_2$ , which has enough electron-donating ligands to compensate for the electron-withdrawing effect of  $\text{C}_{60}$ , can form a stable bisfullerene adduct with a striking feature of a single metal bridging two  $\text{C}_{60}$  cages.<sup>17</sup> Reaction of **10** with excess  $\text{C}_{60}$  in refluxing chlorobenzene, followed by treatment with benzyl isocyanide at room temperature, forms a fullerene–metal cluster sandwich complex,  $\text{Rh}_6(\text{CO})_5(\text{dppm})_2(\text{CNCH}_2\text{C}_6\text{H}_5)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_{60})_2$  (**11**), which is the first example of multiple  $\text{C}_{60}$  coordination on a single metal atom.<sup>17</sup> Compound **11** exhibits two face-capping  $\text{C}_{60}$  ligands on two  $\text{Rh}_3$  triangles, joined by a common Rh metal center, as shown in Figure 4. Although the central rhodium metal atom of the puckered bowtie framework is coordinated by two electron-withdrawing  $\text{C}_{60}$  ligands, the four  $\text{Rh}_{\text{central}}\text{-C}(\text{C}_{60})$  distances (av. 2.17 Å) are comparable to the other eight  $\text{Rh}\text{-C}(\text{C}_{60})$  distances (av. 2.19 Å), implying that the electron density within the cluster unit is highly delocalized. This  $\text{C}_{60}$ –metal cluster sandwich compound should serve as a model compound for two carbon nanotubes connected by a heterogeneous inorganic junction, which might find useful applications in future electronic materials. Closely following our report





<sup>a</sup> R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. Reagents and conditions: (1) RNC, ClC<sub>6</sub>H<sub>5</sub>, 80 °C; (2) (a) Me<sub>3</sub>NO, MeCN/ClC<sub>6</sub>H<sub>5</sub>, RT, (b) PPh<sub>3</sub>, ClC<sub>6</sub>H<sub>5</sub>, 70 °C; (3) CO (2 atm), ClC<sub>6</sub>H<sub>5</sub>, 100 °C; (4) PPh<sub>3</sub>, ClC<sub>6</sub>H<sub>5</sub>, 132 °C.

of the first bisfullerene adduct, Tang et al. reported the preparation of monometallic bisfullerene compounds, [M( $\eta^2$ -C<sub>60</sub>)<sub>2</sub>(CO)<sub>2</sub>(dbcbipy)] (M = W and Mo, dbcbipy = 4,4'-di(butylcarboxyl)-2,2'-bipyridine), in which two trans C<sub>60</sub> ligands bind to a single metal atom in an  $\eta^2$  fashion.<sup>22</sup>

## Ligand-Induced Transformation of C<sub>60</sub> Bonding Modes

**Interconversion between  $\pi$  and  $\sigma$  Bonding Modes.** Reaction of Os<sub>3</sub>(CO)<sub>8</sub>(CNR)( $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ -C<sub>60</sub>) (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (**12**) and CNR at 80 °C in chlorobenzene forms two isomeric  $\sigma$ - $\pi$  mixed type compounds, Os<sub>3</sub>(CO)<sub>8</sub>(CNR)( $\mu_3$ -CNR)( $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$ -C<sub>60</sub>) (**13a,b**) (Scheme 3).<sup>23</sup> The external CNR ligand inserts into an Os–Os bond to give a bent Os<sub>3</sub> framework and coordinates to the three osmium metal centers via a 4e-donor  $\mu_3$ - $\eta^2$  bonding mode. The other terminal isocyanide ligand occupies an equatorial position at the central osmium atom for **13a** and at the terminal osmium atom for **13b**.

Figure 5 shows the molecular structure of **13a**, which is the first structurally characterized C<sub>60</sub>–metal  $\sigma$ -complex. The two outer osmium atoms coordinate to the C1 and C4 atoms of the C<sub>60</sub> ligand in a  $\sigma$  fashion, respectively, while the central osmium atom is  $\pi$ -coordinated to the C2 and C3 atoms in an  $\eta^2$  mode. The two Os–C (C<sub>60</sub>)  $\sigma$ -bonds (2.25 and 2.26 Å) are shorter than the Os–C<sub>2</sub>  $\pi$ -interaction (av. 2.42 Å). The bond lengths of C2–C3 (1.44 Å) and C5–C6 (1.36 Å) reveal double bond character, and the other four C–C bonds (av. 1.52 Å) exhibit single bond character. In **13a**, the sums of three angles around sp<sup>3</sup>-hybridized carbons (328° and 327°) are considerably smaller than those (av. 351°) for the other four carbon atoms with a sp<sup>2</sup> hybridization. Thus, the two sp<sup>3</sup>-hybridized carbon atoms (C1 and C4) are pulled away

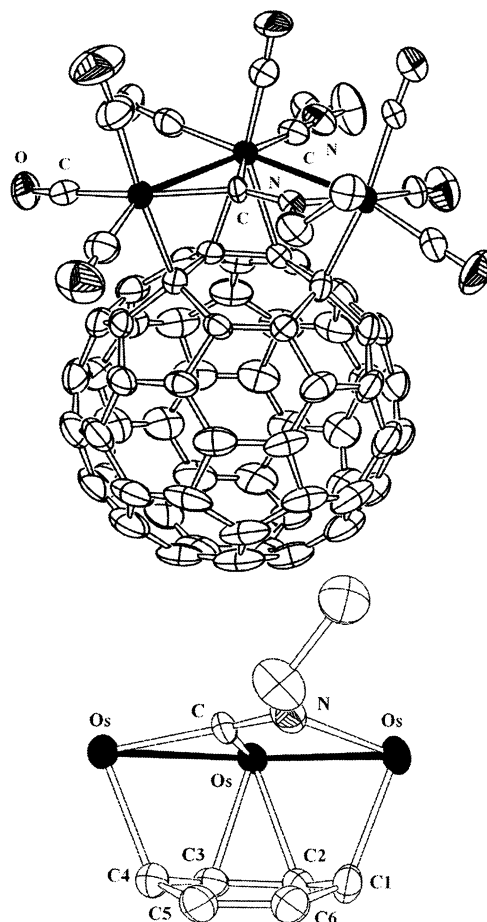


FIGURE 5. Molecular structure of **13a**. Phenyl groups except ipso-carbons are removed for clarity.

from the smooth curvature of the C<sub>60</sub> ligand, which is manifested by the boat shape of the C<sub>6</sub>-ring, with sp<sup>3</sup>-hybridized carbon atoms at the bow and stern positions, as shown in Figure 5. The general structural features of **13b** are similar to those of **13a**.

The cyclohexatriene-like C<sub>6</sub>-ring of C<sub>60</sub> in **12** has undergone orbital reorganization to form a 1,4-cyclohexadiene-like ring in **13a** and **13b**. It can be envisaged that the 4e-donor CNR ligand formally provides two electrons to the antibonding orbital of an Os–Os interaction in **12**, resulting in the scission of the Os–Os bond. The remnant two electrons from the CNR ligand interrupt two  $\pi$ -interactions in **12** to give two Os–C (C<sub>60</sub>)  $\sigma$ -bonds and an uncoordinated C=C bond in **13a** and **13b**. The 1,4-addition isomer of C<sub>60</sub>–metal  $\sigma$ -complexes has been proposed previously in a few cases, such as in C<sub>60</sub>{Re(CO)<sub>5</sub>}<sub>2</sub> and C<sub>60</sub>{Mo(CO)<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Et)}<sub>2</sub>.<sup>24</sup>

While thermal reaction of **12** with CNR produces a mixture of **13a** and **13b**, photolysis reaction of **12** with CNR by a medium-pressure Hg lamp selectively affords **13b**. Compounds **13a** and **13b** are not interconvertible either under irradiation or at elevated temperatures, which eliminates the possibility of interconversion between **13a** and **13b** by intermetallic movement of the terminal CNR ligand. The diradical species formed by homolytic cleavage of an Os–Os bond of **12** under photochemical conditions

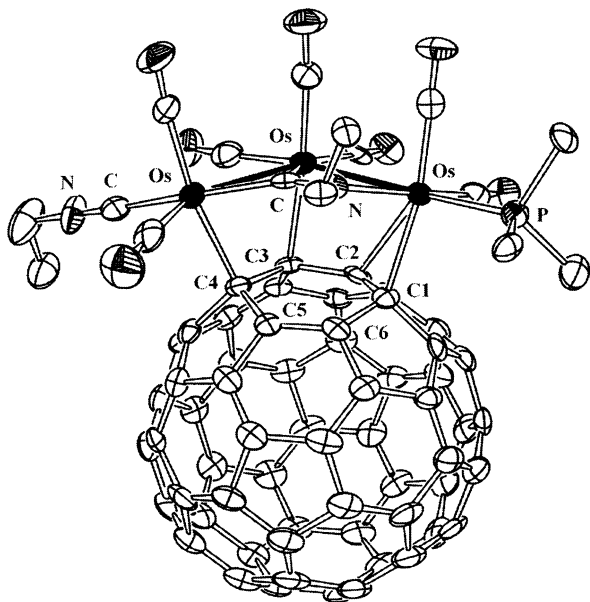


FIGURE 6. Molecular structure of **14**. Phenyl groups except ipso-carbons are removed for clarity.

is likely to be stabilized by the donor property of the terminal CNR ligand, to result in the selective formation of **13b**.

Decarbonylation of **13b** with Me<sub>3</sub>NO/MeCN and subsequent reaction with PPh<sub>3</sub> produces Os<sub>3</sub>(CO)<sub>7</sub>(CNR)(μ<sub>3</sub>-CNR)(PPh<sub>3</sub>)(μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>-C<sub>60</sub>) (**14**), in which the PPh<sub>3</sub> ligand occupies an equatorial position of a terminal osmium atom by replacing a carbonyl ligand (Figure 6).<sup>25</sup> The μ<sub>3</sub>-η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>-C<sub>60</sub> (1,4-disubstituted cyclohexadiene-like C<sub>6</sub>-ring) moiety in **13b** has undergone further orbital rearrangement to form the μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>-C<sub>60</sub> (1,2-disubstituted cyclohexadiene-like C<sub>6</sub>-ring) ligand (Scheme 3). The two Os–C (C<sub>60</sub>) σ-bonds (2.24, 2.25 Å) are shorter than the π-bond (av. 2.45 Å), as previously observed in **13a** and **13b**. The bond lengths of C1–C2 (1.43 Å) and C5–C6 (1.39 Å) reveal double bond character, and the other four C–C bonds (av. 1.51 Å) show single bond character, clearly indicating the 1,3-cyclohexadiene nature of the C<sub>6</sub>-ring of C<sub>60</sub>. While the bulky PPh<sub>3</sub> ligand is coordinated at the less hindered outer osmium site, a similar reaction with PMe<sub>3</sub> produces Os<sub>3</sub>(CO)<sub>7</sub>(CNR)(μ<sub>3</sub>-CNR)(PMe<sub>3</sub>)(μ<sub>3</sub>-η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>-C<sub>60</sub>) (**15**), in which the smaller PMe<sub>3</sub> ligand merely substitutes an axial carbonyl ligand on a central osmium atom without changing the C<sub>60</sub> bonding mode. The metal center coordinated by the donor phosphine ligand apparently prefers a π-interaction with C<sub>60</sub> because of back-donation from the metal to C<sub>60</sub>. The PPh<sub>3</sub> ligand is easily replaced by CO to result in clean conversion of **14** to **13b**, which represents a reversible interconversion between the μ<sub>3</sub>-η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>-C<sub>60</sub> and μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>-C<sub>60</sub> bonding modes.

Further interaction of **14** with PPh<sub>3</sub> at an elevated temperature forms a π-type complex, Os<sub>3</sub>(CO)<sub>6</sub>(CNR)(μ<sub>3</sub>-CNCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)(μ-PPh<sub>2</sub>)(μ-η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub>) (**16**), in which the C<sub>60</sub> ligand has regained the cyclohexatriene-like C<sub>6</sub>-ring hybridization (Scheme 3).<sup>25</sup> One Os–Os bond in **14** is ruptured, and the two intact osmium metals are bridged by a μ-η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub> ligand. The bridging isocyanide ligand is

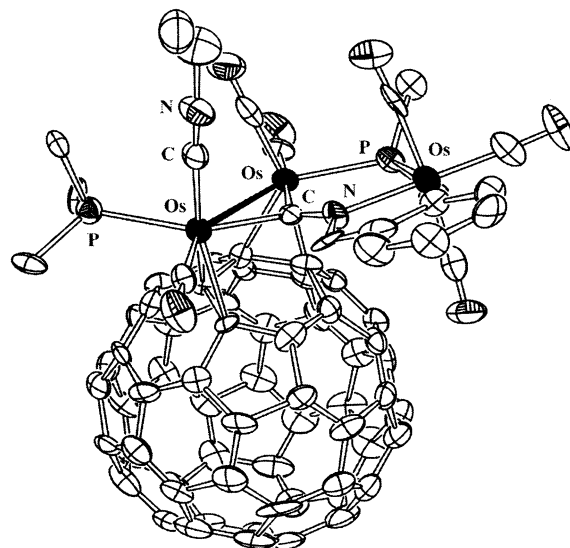
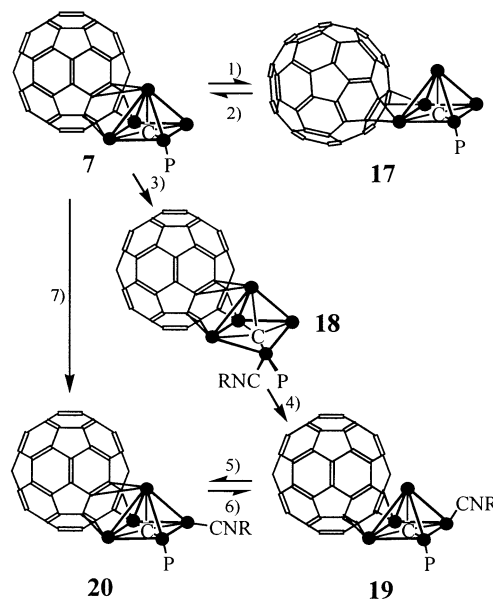


FIGURE 7. Molecular structure of **16**. Phenyl groups except ipso-carbons are removed for clarity.

#### Scheme 4<sup>a</sup>

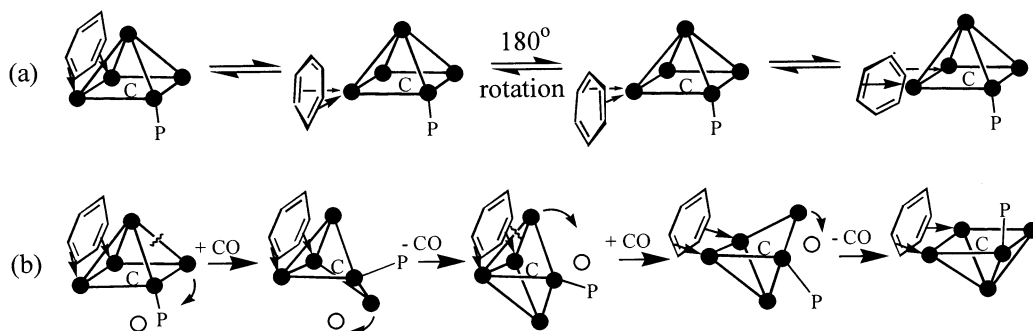


<sup>a</sup> R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, P = PPh<sub>3</sub>. Reagents and conditions: (1) CO (1 atm), ClC<sub>6</sub>H<sub>5</sub>, 80 °C; (2) ClC<sub>6</sub>H<sub>5</sub>, 132 °C; (3) RNC, ClC<sub>6</sub>H<sub>5</sub>, RT; (4) ClC<sub>6</sub>H<sub>5</sub>, 100 °C; (5) Me<sub>3</sub>NO, MeCN/ClC<sub>6</sub>H<sub>5</sub>, RT; (6) ClC<sub>6</sub>H<sub>5</sub>, 132 °C; (7) CO (3 atm), ClC<sub>6</sub>H<sub>5</sub>, 55 °C; (7) excess Ph<sub>3</sub>P=NCH<sub>2</sub>Ph, ClC<sub>6</sub>H<sub>5</sub>, RT.

bonded to all three Os centers, but the phenyl group orthometalates to the released osmium atom, forming a five-membered metalacycle (OsNC<sub>3</sub>), as shown in Figure 7. A benzene molecule, formed by coupling of a hydride from the orthometalation and a phenyl group from PPh<sub>3</sub>, is dissociated from the molecule to give the μ-PPh<sub>2</sub> moiety.

**Reversible Interconversion between μ-η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub> and μ<sub>3</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub>.** Os<sub>5</sub>C(CO)<sub>11</sub>(PPh<sub>3</sub>)(μ<sub>3</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub>) (**7**) reacts with CO to form Os<sub>5</sub>C(CO)<sub>12</sub>(PPh<sub>3</sub>)(μ-η<sup>2</sup>:η<sup>2</sup>-C<sub>60</sub>) (**17**), in which two adjacent double bonds in a C<sub>6</sub>-ring of C<sub>60</sub> bridge the two basal osmium atoms (Scheme 4).<sup>15,16</sup> The third uncoordinated double bond in the C<sub>6</sub>-ring of **17** is placed away from the Os<sub>3</sub> triangle; the C<sub>60</sub> ligand apparently rotates by 180° during the conversion of **7** to **17**. A similar

Scheme 5



$\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  bonding mode with two metal centers has been previously reported for dinuclear metal compounds such as  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})[\text{Ir}_2\text{Cl}_2(1,5\text{-COD})_2]_2$ ,  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})[\text{Cp}'_2\text{Ru}_2(\mu\text{-Cl})_2]$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ ), and  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})[\text{Re}_2\text{H}_8(\text{PMe}_3)_4]$ .<sup>6</sup> Thermolysis of **17** results in loss of a carbonyl ligand, C<sub>60</sub> rotation by 180°, and re-formation of a Os–C<sub>2</sub> (C<sub>60</sub>) bond to give **7**, which demonstrates a reversible interconversion between  $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  and  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$ .<sup>15,16</sup>

The reaction pathways for the reversible interconversion between **7** and **17** have been investigated by a labeling study with a benzyl isocyanide ligand, CNR ( $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ ). The reaction of **7** with CNR at room temperature results in an addition product,  $\text{Os}_5\text{C}(\text{CO})_{11}(\text{PPh}_3)(\text{CNR})(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60})$  (**18**), in which the  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$  bonding mode is unaffected, but one of the Os<sub>apical</sub>–Os<sub>basal</sub> bonds in the square-pyramidal Os<sub>5</sub>C framework is cleaved to form a “wing-tip-bridged butterfly” framework.<sup>15,16</sup> The kinetic product **18** is transformed to a thermodynamic isomer,  $\text{Os}_5\text{C}(\text{CO})_{11}(\text{PPh}_3)(\text{CNR})(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$  (**19**), at 100 °C; an Os–Os bond is re-formed between the bridged and “hinge” osmium atoms, followed by CNR ligand migration to an adjacent basal Os atom and removal of the Os<sub>apical</sub>–C<sub>2</sub> (C<sub>60</sub>) interaction.<sup>15,16</sup> In this transformation, the C<sub>60</sub> rotation does not take place, unlike the interconversion between **7** and **17**. Decarbonylation of **19** with Me<sub>3</sub>NO/MeCN and subsequent heating results in the formation of  $\text{Os}_5\text{C}(\text{CO})_{10}(\text{PPh}_3)(\text{CNR})(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60})$  (**20**), which can be reconverted to **19** by interaction with CO, revealing another example of the reversible interconversion between  $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  and  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$  on a cluster framework.<sup>16</sup>

The origin of the disparity in the placement of the  $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  ligand in **17** and **19** seems to be electronic, since the steric environment around the C<sub>60</sub> ligand appears to be essentially identical in both compounds. Two plausible mechanisms can be proposed to explain the 180° rotation in the conversion of **7** to **17**. One obvious possibility would be a 180° rotation of the C<sub>60</sub> ligand with the cluster core intact, via pathways of  $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  to  $\eta^4\text{-C}_{60}$  and to  $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$ , as shown in Scheme 5a. Even though the  $\eta^4\text{-C}_{60}$  bonding mode has yet to be discovered, the  $\eta^4$ -cyclohexadiene moiety on a metal center has been well documented for Os<sub>3</sub> cluster compounds.<sup>26</sup> The other mechanism, hinted at by the isocyanide ligand addition reaction of **7**, would be a metal framework rearrangement, which involves a series of Os–Os bond scissions and formations

to invert the square-pyramidal Os<sub>5</sub>C cluster framework (Scheme 5b). In this “octahedral site exchange” mechanism, a carbonyl addition induces an Os–Os bond scission to give a bridged “butterfly” intermediate analogous to **18**, where the bridging osmium center moves into an empty vertex of an imaginary octahedron to form a half-inverted square-pyramidal geometry. Repeating similar processes may produce the inverted product. A similar cluster framework rearrangement was observed in a related arene cluster compound,  $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ .<sup>27</sup>

## Electrochemical Properties

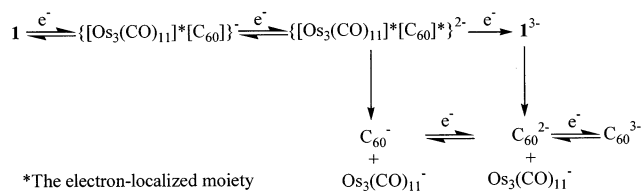
Free C<sub>60</sub> is known to be fairly electronegative, being reducible up to C<sub>60</sub><sup>6−</sup> due to its triply degenerate LUMO.<sup>28</sup> Electrochemical studies of monometallic C<sub>60</sub> derivatives such as  $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})(\eta^2\text{-C}_{60})$ <sup>29</sup> and  $(\text{Et}_3\text{P})_2\text{M}(\eta^2\text{-C}_{60})$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ )<sup>30</sup> have revealed C<sub>60</sub>-localized sequential reductions and their electrochemical instability upon reduction. Half-wave potentials ( $E_{1/2}$ ) observed in cyclic voltammetric studies are summarized in Table 1 for free C<sub>60</sub> and for various triosmium and trirhenium cluster complexes with  $\eta^2\text{-C}_{60}$  and  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$  ligands. The first reduction wave of  $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_{60})$  (**1**), at  $E_{1/2} = -1.08$  V, is slightly more negative than that of free C<sub>60</sub>, at  $E_{1/2} = -1.05$  V,<sup>19</sup> which is consistent with metal-to-C<sub>60</sub>  $\pi$ -back-donation, as was shown in other monometallic C<sub>60</sub> complexes.<sup>29,30</sup> However, the second and third reductions appear at potentials more positive by 0.10 and 0.29 V, respectively, than those of free C<sub>60</sub>. This unusual anodic shifts and the IR spectroelectrochemical study of **1** imply that the first electron accepted via the C<sub>60</sub> ligand in **1** is delocalized to the triosmium center with its strong  $\pi$ -acid carbonyl ligands, as shown in Scheme 6.<sup>19</sup> The first reduction potentials of phosphine-substituted  $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)(\eta^2\text{-C}_{60})$  (**21**) and  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$  (**22**) are further shifted to potentials more negative relative to **1** by 0.08 and 0.11 V, respectively, reflecting the electron-donating nature of the phosphine ligands. The anodic shifts of the third reduction potentials of **21** (0.22 V) and **22** (0.14 V) compared to that of free C<sub>60</sub> reveal that a similar C<sub>60</sub>-mediated electron delocalization occurs in **21**<sup>2−</sup> and **22**<sup>2−</sup> species. Reduced species of **1**, **21**, and **22** undergo fast decomposition, as shown in Scheme 6, and thus detailed electrochemical studies are precluded for  $\eta^2\text{-C}_{60}$  cluster complexes.



**Table 1. Half-Wave Potentials ( $E_{1/2}$  vs  $E_{\text{Fc/Fc}^+}^0$ ) of Free  $\text{C}_{60}$  and Various  $\eta^2\text{-C}_{60}$  and  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  Metal Clusters**

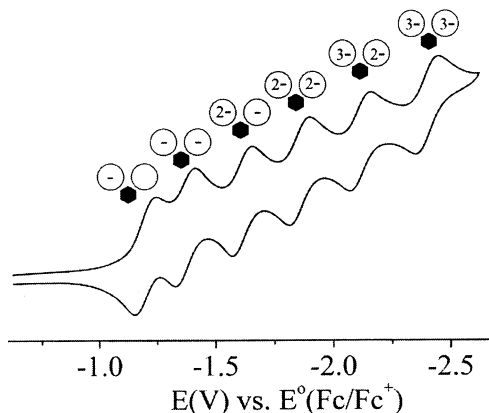
compound	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	$E_{1/2}^{-3/-4}$	solvent	ref
$\text{C}_{60}$	-1.05 (-1.08)	-1.41 (-1.44)	-1.87 (-1.90)		DM/Tol	19
$\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_{60})$ ( <b>1</b> )	-1.08 (-1.12)	-1.31 (-1.34)	<i>b</i> (-1.61)		DM/Tol	19
$\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ ( <b>21</b> )	-1.16 (-1.18)	-1.44 (-1.49)	<i>b</i> (-1.68)		DM/Tol	19
$\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$ ( <b>22</b> )	-1.19 (-1.21)	-1.53 (-1.56)	<i>b</i> (-1.76)		DM/Tol	19
$\text{C}_{60}$	-1.08	-1.46	-1.90	-2.38	DCB	11
$\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$ ( <b>2</b> )	-0.98	-1.33	-1.61	-1.74	DCB	11
$\text{Os}_3(\text{CO})_8(\text{PMe}_3)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$	-1.06	-1.42	-1.93	-1.95	DCB	11
$\text{Os}_3(\text{CO})_7(\text{PMe}_3)_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$	-1.13	-1.48	-2.09		DCB	11
$\text{C}_{60}$	-1.06	-1.43	-1.91	-2.38	CB	7
$\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$ ( <b>4</b> )	-0.95	-1.24	-1.34	-1.73	CB	7
$\text{Re}_3(\mu\text{-H})_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$	-1.04	-1.35	-1.75	-1.77	CB	7

<sup>a</sup> The cathodic peak potentials ( $E_{\text{pc}}$ ) at the scan rate of 20.5 V/s are given in parentheses. <sup>b</sup> Half-wave potentials could not be obtained due to very fast decomposition of  $\mathbf{1}^{3-}$ ,  $\mathbf{21}^{3-}$ , and  $\mathbf{22}^{3-}$ .

**Scheme 6**

On the other hand, the  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$  metal cluster complexes show reversible redox waves within the solvent cutoff and remarkable electrochemical stabilities. The  $\text{C}_{60}$ -localized first and second reduction waves of  $\text{Os}_3(\text{CO})_9\text{-}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$  (**2**) and  $\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$  (**4**) are shifted to more positive potentials by 0.10 and 0.13 V and by 0.11 and 0.19 V, respectively, in comparison with those of free  $\text{C}_{60}$ .<sup>7,11</sup> This anodic shift may be ascribed to the inductive effect of the metal carbonyl cluster adds on the stabilization of the  $\text{C}_{60}$ -localized LUMO. The anodic shifts of the third and fourth waves of **2** (0.29, 0.64 V) and **4** (0.57, 0.65 V) are even more pronounced, which suggests that the electron density in  $\mathbf{2}^{2-}$ ,  $\mathbf{2}^{3-}$ ,  $\mathbf{4}^{2-}$ , and  $\mathbf{4}^{3-}$  is significantly delocalized to the metal cluster center. A theoretical study on the ruthenium analogue **3** seems to support our electrochemical data.<sup>31</sup> While the first two reductions place electrons in the mostly  $\text{C}_{60}$ -based LUMO, the two LUMO + 1 orbitals contain some  $\text{Ru}_3(\text{CO})_9$  character and thus allow electron delocalization into the cluster moiety.<sup>31</sup> Substitution of phosphine ligands in **2** and **4** not only results in cathodic shifts of reduction potentials due to the donating property of the ligands, but also influences the overall electrochemical behavior of the  $\text{C}_{60}$  complexes, as shown in Table 1. Similar  $\text{C}_{60}$ -mediated electron delocalization into the cluster moiety and phosphine ligand-induced cathodic shifts of reduction potentials were also observed for  $\text{Ru}_5\text{C-C}_{60}$  and  $\text{PtRu}_5\text{C-C}_{60}$  clusters.<sup>32</sup> This observation promises an important possibility that the electronic properties of  $\text{C}_{60}$ -metal cluster complexes can be fine-tuned by modification in the coordination sphere of the metal cluster moieties.

Bisfullerene compounds have received considerable attention due to their potential for future optical and electronic applications.<sup>33</sup> In the cases of organic bisfullerene compounds, a weak, through-space electronic communication between  $\text{C}_{60}$  cages has been observed only for  $\text{C}_{120}\text{O}$ ,<sup>34</sup>  $\text{C}_{120}(\text{CH}_2)_2$ ,<sup>35</sup> and  $\text{C}_{120}\text{C}$ ,<sup>36</sup> where the fullerenes

**FIGURE 8.** Cyclic voltammogram of **11** (Scan rate = 10 mV/s).

are directly bonded to each other or are separated by a single carbon spacer. The intercage electronic communication can be dramatically increased by the presence of a metal cluster spacer. The cyclic voltammogram (CV) of  $\text{Rh}_6(\text{CO})_5(\text{dppm})_2(\text{CNCH}_2\text{C}_6\text{H}_5)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})_2$  (**11**) exhibits six well-separated reversible, one-electron redox waves localized at  $\text{C}_{60}$  cages (Figure 8).<sup>17</sup> Each redox wave of **11** corresponds to sequential, pairwise addition of six electrons into the two  $\text{C}_{60}$  centers to form  $\text{C}_{60}^-\text{-Rh}_6\text{-C}_{60}$ ,  $\text{C}_{60}^{2-}\text{-Rh}_6\text{-C}_{60}$ ,  $\text{C}_{60}^{3-}\text{-Rh}_6\text{-C}_{60}$ , ..., and ultimately  $\text{C}_{60}^{3-}\text{-Rh}_6\text{-C}_{60}^{3-}$ . The electronic environment for the two  $\text{C}_{60}$  centers in **11** is very similar despite the difference in coordination spheres around the two  $\text{C}_{60}$  centers, since there is little difference between donor effects of a phosphine ligand and a benzyl isocyanide ligand in  $\text{C}_{60}$ -metal cluster complexes.<sup>17</sup> Therefore, the large peak separations [ $\Delta(E_{1/2}^1, E_{1/2}^2) = 0.19$  V,  $\Delta(E_{1/2}^3, E_{1/2}^4) = 0.24$  V, and  $\Delta(E_{1/2}^5, E_{1/2}^6) = 0.29$  V] in the three redox pairs of the two  $\text{C}_{60}$  ligands reflect an unusually strong electronic communication between the two  $\text{C}_{60}$  centers via the  $\text{Rh}_6$  spacer. In compound **11**, the long distance (3.55 Å) between the two  $\text{C}_{60}$  centers limits  $\pi$ -orbital overlap of separate  $\text{C}_{60}$  cages, and thus contribution of the through-space electronic communication is expected to be negligible. The second redox wave in each pair in the CVs of **11** becomes increasingly separated from the first wave as the reduction proceeds, presumably due to the effects of increasing Coulombic repulsion between the two  $\text{C}_{60}$  moieties.

## Concluding Remarks

[60]Fullerene can bind a variety of metal clusters via  $\eta^2$ - $C_{60}$ ,  $\mu$ - $\eta^2$ : $\eta^2$ - $C_{60}$ , and  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$   $\pi$ -type bonding modes, acting as 2e-, 4e-, and 6e-donor ligands. Interestingly, modification of the coordination sphere of  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  metal cluster complexes results in new bonding modes, such as  $\pi$ -type  $\mu$ - $\eta^2$ : $\eta^2$ - $C_{60}$  and  $\sigma$ - $\sigma$  mixed types  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$ - and  $\mu_3$ - $\eta^1$ : $\eta^1$ : $\eta^2$ - $C_{60}$ , where  $C_{60}$  is a 4e-donor ligand. Such a facile orbital rehybridization on a cluster core provides a new synthetic route to  $C_{60}$ –metal  $\sigma$ -complexes, which are very important in selective functionalization of  $C_{60}$ . The  $C_{60}$ –metal cluster complexes reveal an unusual electronic communication between  $C_{60}$  and metal cluster moieties. In particular, the effective overlap of  $C_{60}$  p- $\pi$  orbitals and metal d- $\pi$  orbitals in  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  metal cluster complexes leads to a remarkable electrochemical stability of the reduced states and a strong electrochemical interaction between  $C_{60}$  and cluster centers as well as between two  $C_{60}$  cages bridged by a metal cluster spacer. The electronic properties of  $C_{60}$ –metal cluster complexes can be readily fine-tuned by modification of the ligands of metal cluster moieties. Further development in  $C_{60}$ –metal cluster chemistry, utilizing a number of available cluster systems, would undoubtedly result in not only the discovery of new interaction types between  $C_{60}$  and metal surfaces but also practical applications of this unique family of  $C_{60}$ –metal cluster compounds in electronic device fabrication.

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## References

- Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Solid  $C_{60}$ : a new form of carbon. *Nature* **1990**, *347*, 354–358.
- (a) Wudl, F. The Chemical Properties of Buckminsterfullerene ( $C_{60}$ ) and the Birth and Infancy of Fullerenoids. *Acc. Chem. Res.* **1992**, *25*, 157–161. (b) Hirsch, A. The Chemistry of the Fullerenes; Thieme: New York, 1994. (c) Diederich, F.; Thilgen, C. Covalent Fullerene Chemistry. *Science* **1996**, *271*, 317–323. (d) Taylor, R. *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*; Imperial College Press: London, 1999.
- (a) Stephens, A.; Green, M. L. H. Organometallic Complexes of Fullerenes. *Adv. Inorg. Chem.* **1997**, *44*, 1–43. (b) Mathur, P.; Mavunkal, I. J.; Umbarkar, S. B. Synthetic Methodologies and Structures of Metal- $[C_{60}]$  Fullerene Complexes. *J. Cluster Sci.* **1998**, *9*, 393–415. (c) Balch, A. L.; Olmstead, M. M. Reactions of Transition Metal Complexes with Fullerenes ( $C_{60}$ ,  $C_{70}$ , etc.) and Related Materials. *Chem. Rev.* **1998**, *98*, 2123–2165.
- (a) Govindaraj, A.; Satishkumar, B. C.; Nath, M.; Rao, C. N. R. Metal Nanowires and Intercalated Metal Layers in Single-Walled Carbon Nanotube Bundles. *Chem. Mater.* **2000**, *12*, 202–205. (b) Hermans, S.; Sloan, J.; Shephard, D. S.; Johnson, B. F. G.; Green, M. L. H. Bimetallic nanoparticles aligned at the tips of carbon nanotubes. *Chem. Commun.* **2002**, 276–277.
- (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. The Chemical Nature of Buckminsterfullerene ( $C_{60}$ ) and the Characterization of a Platinum Derivative. *Science* **1991**, *252*, 1160–1161. (b) Balch, A. L.; Catalano, V. J.; Lee, J. W. Accumulating Evidence for the Selective Reactivity of the 6–6 Ring Fusion of  $C_{60}$ . Preparation and Structure of  $(\eta^2-C_{60})Ir(CO)Cl(PPh_3)_2 \cdot 5C_6H_6$ . *Inorg. Chem.* **1991**, *30*, 3980–3981. (c) Koefod, R. S.; Hudgens, M. F.; Shapley, J. R. Organometallic Chemistry with Buckminsterfullerene. Preparation and Properties of an Indenyliridium(I) Complex. *J. Am. Chem. Soc.* **1991**, *113*, 8957–8958. (d) Fagan, P. J.; Calabrese, J. C.; Malone, B. A Multiply-Substituted Buckminsterfullerene ( $C_{60}$ ) with an Octahedral Array of Platinum Atoms. *J. Am. Chem. Soc.* **1991**, *113*, 9408–9409. (e) Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. Transition Metal–carbonyl, –hydrido and – $\eta$ -Cyclopentadienyl Derivatives of the Fullerene  $C_{60}$ . *Chem. Commun.* **1993**, 1522–1523. (f) Bashilov, V. V.; Petrovskii, P. V.; Sokolov, V. I.; Lindeman, S. V.; Guzey, I. A.; Struchkov, Y. T. Synthesis, Crystal, and Molecular Structure of the Palladium(0)-Fullerene Derivative  $(\eta^2-C_{60})Pd(PPh_3)_2$ . *Organometallics* **1993**, *12*, 991–992. (g) Balch, A. L.; Lee, J. W.; Noll, N. C.; Olmstead, M. M. Structural Characterization of  $\{(\eta^2-C_{60})Rh(CO)(PPh_3)_2\}$ : Product of the Reaction of  $C_{60}$  with the Hydrogenation Catalyst  $\{Rh(CO)(PPh_3)_2\}$ . *Inorg. Chem.* **1993**, *32*, 3577–3578. (h) Hsu, H.-F.; Du, Y.; Albrecht-Schmitt, T. E.; Wilson, S. R.; Shapley, J. R. Structural Comparison of  $M(CO)_3(dppe)(\eta^2-C_{60})$  ( $M = Mo, W$ ),  $Mo(CO)_3(dppe)(\eta^2-C_{70})$ , and  $W(CO)_3(dppe)(\eta^2-trans-C_2H_2(CO_2Me)_2)$ . *Organometallics* **1998**, *17*, 1756–1761.
- (a) Rasinkangas, M.; Pakkanen, T. T.; Pakkanen, T. A.; Ahlgrén, M.; Rouvinen, J. Multimetallic Binding to Fullerenes:  $C_{60}\{Ir_2Cl_2(1,5-COD)_2\}_2$ . A Novel Coordination Mode to Fullerenes. *J. Am. Chem. Soc.* **1993**, *115*, 4901. (b) Mavunkal, I. J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. Preparation and Structure of  $Cp^*_2Ru_2(\mu-Cl)(\mu-X)(C_{60})$ ,  $X = H$  and  $Cl$ . Novel Dinuclear Fullerene Complexes with and without Direct Ruthenium–Ruthenium Bonding. *Organometallics* **1995**, *14*, 4454–4456. (c) Chernega, A. N.; Green, M. L. H.; Haggitt, J.; Stephens, A. H. H. New Transition-metal Derivatives of the Fullerene  $C_{60}$ . *J. Chem. Soc., Dalton Trans.* **1998**, 755–767.
- Song, H.; Lee, Y.; Choi, Z.-H.; Lee, K.; Park, J. T.; Kwak, J.; Choi, M.-G. Synthesis and Characterization of  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  Triruthenium Hydrido Cluster Complexes. *Organometallics* **2001**, *20*, 3139–3144.
- Hsu, H.-F.; Shapley, J. R.  $Ru_3(CO)_5(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ : A Cluster Face-Capping, Arene-Like Complex of  $C_{60}$ . *J. Am. Chem. Soc.* **1996**, *118*, 9192–9193.
- Hsu, H.-F.; Shapley, J. R. Triruthenium cluster complexes of  $C_{60}$  and  $C_{70}$ : Carbonyl site exchange probed via triphenylphosphine ligand derivatives. *J. Organomet. Chem.* **2000**, *599*, 97–105.
- Park, J. T.; Song, H.; Cho, J.-J.; Chung, M.-K.; Lee, J.-H.; Suh, I.-H. Synthesis and Characterization of  $\eta^2$ - $C_{60}$  and  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  Triosmium Cluster Complexes. *Organometallics* **1998**, *17*, 227–236.
- Song, H.; Lee, K.; Park, J. T.; Choi, M.-G. Synthesis, Structure, and Electrochemical Studies of  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  Triosmium Complexes. *Organometallics* **1998**, *17*, 4477–4483.
- Song, H.; Lee, K.; Park, J. T.; Chang, H. Y.; Choi, M.-G. Fluxional processes and structural characterization of  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  triosmium cluster complexes,  $Os_3(CO)_9-n(PMe_3)_n(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$  ( $n = 1, 2, 3$ ). *J. Organomet. Chem.* **2000**, *599*, 49–56.
- Lee, K.; Hsu, H.-F.; Shapley, J. R. Coordination of  $C_{60}$  to Penta- and Hexaruthenium Cluster Frames. *Organometallics* **1997**, *16*, 3876–3877.
- Lee, K.; Shapley, J. R. Face-Coordinated  $C_{60}$  Complexes with Carbido Pentaruthenium Cluster Cores Including a Bimetallic Platinum–Pentaruthenium Complex. *Organometallics* **1998**, *17*, 3020–3026.
- Lee, K.; Lee, C. H.; Song, H.; Park, J. T.; Chang, H. Y.; Choi, M.-G. Interconversion between  $\mu$ - $\eta^2$ : $\eta^2$ - $C_{60}$  and  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  on a Carbido Pentaosmium Cluster Framework. *Angew. Chem., Int. Ed.* **2000**, *39*, 1801–1804.
- Lee, K.; Choi, Z.-H.; Cho, Y.-J.; Song, H.; Park, J. T. Reversible Interconversion between  $\mu$ - $\eta^2$ : $\eta^2$ - $C_{60}$  and  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$ - $C_{60}$  on a Carbido Pentaosmium Cluster Framework. *Organometallics* **2001**, *20*, 5564–5570.
- Lee, K.; Song, H.; Kim, B.; Park, J. T.; Park, S.; Choi, M.-G. The First Fullerene-Metal Sandwich Complex: An Unusually Strong Electronic Communication between Two  $C_{60}$  Cages. *J. Am. Chem. Soc.* **2002**, *124*, 2872–2873.
- Park, J. T.; Cho, J.-J.; Song, H. Triosmium Cluster Derivatives of [60]Fullerene. *Chem. Commun.* **1995**, 15–16.
- Park, J. T.; Cho, J.-J.; Song, H.; Jun, C.-S.; Son, Y.; Kwak, J. Electrochemical Studies of  $C_{60}$ –Triosmium Complexes: First Evidence for a  $C_{60}$ -Mediated Electron Transfer to the Metal Center. *Inorg. Chem.* **1997**, *36*, 2698–2699.
- Haddon, R. C.  $\pi$ -Electrons in Three Dimensions. *Acc. Chem. Res.* **1988**, *21*, 243–249.
- Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. Arene Clusters. *Chem. Rev.* **1994**, *94*, 1585–1620.
- Jin, X.; Xie, X.; Tang, K. Syntheses and X-ray crystal structures of dumbbell-shaped bis-fullerene tungsten and molybdenum complexes. *Chem. Commun.* **2002**, 750–751.
- (a) Song, H.; Lee, K.; Lee, C. H.; Park, J. T.; Chang, H. Y.; Choi, M.-G. First Example of the  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$ - $C_{60}$  Bonding Mode: Ligand-Induced Conversion of  $\pi$  to  $\sigma$   $C_{60}$ –Metal Complexes. *Angew.*



- Chem., Int. Ed.* **2001**, *40*, 1500–1502. (b) Song, H.; Lee, C. H.; Lee, K.; Park, J. T. Ligand Induced Conversion of  $\pi$  to  $\sigma$  C<sub>60</sub>–Metal Cluster Complexes: Full Characterization of  $\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^1\text{-C}_{60}$  Bonding Mode. *Organometallics* **2002**, *21*, 2514–2520.
- (24) (a) Zhang, S.; Brown, T. L.; Du, Y.; Shapley, J. R. Metalation of C<sub>60</sub> with Pentacarbonylrhenium Radicals. Reversible Formation of C<sub>60</sub>{Re(CO)<sub>5</sub>}<sub>2</sub>. *J. Am. Chem. Soc.* **1993**, *115*, 6705–6709. (b) Zhu, Y.-H.; Song, L.-C.; Hu, Q.-M.; Li, C.-M. Synthesis and Isolation of  $\sigma$ -Bonded Fullerene Metal Derivatives from Reactions of Fullerene Dianion C<sub>60</sub><sup>2-</sup> with Organometal Halides. *Org. Lett.* **1999**, *1*, 1693–1695.
- (25) Song, H.; Lee, K.; Choi, M.-G.; Park, J. T. [60] Fullerene as a Versatile Four-electron Donor Ligand. *Organometallics* **2002**, *21*, 1756–1758.
- (26) (a) Blake, A. J.; Dyson, P. J.; Johnson, B. F. G.; Martin, C. M.; Nairn, J. G. M.; Parisini, E.; Lewis, J. New Synthetic Routes to [M<sub>3</sub>(CO)<sub>9</sub>( $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6$ )] M = Ru or Os). *J. Chem. Soc., Dalton Trans.* **1993**, 981–984. (b) Braga, D.; Grepioni, F.; Parisini, E.; Johnson, B. F. G.; Martin, C. M.; Nairn, J. G. M.; Lewis, J.; Martinelli, M. Synthesis of [M<sub>3</sub>H(CO)<sub>9</sub>( $\mu_3\text{-}\sigma\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_7$ )] (M = Ru or Os). Molecular and Crystal Structure of the Ruthenium Cluster. *J. Chem. Soc., Dalton Trans.* **1993**, 1891–1895.
- (27) Braga, D.; Grepioni, F.; Sabatino, P.; Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Bailey, P. J.; Raithby, P. R.; Stalke, D. Synthesis and Structural Characterization of Diene and Benzene Pentaruthenium Clusters. *J. Chem. Soc., Dalton Trans.* **1993**, 985–992.
- (28) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. Electrochemical Detection of C<sub>60</sub><sup>6-</sup> and C<sub>70</sub><sup>6-</sup>: Enhanced Stability of Fullerides in Solution. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.
- (29) Koefod, R. S.; Xu, C.; Lu, W.; Shapley, J. R.; Hill, M. G.; Mann, K. R. An Electrochemical Study of an Iridium–Buckminsterfullerene Complex. Evidence for C<sub>60</sub>-Localized Reductions. *J. Phys. Chem.* **1992**, *96*, 2928–2930.
- (30) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. Electrochemical Studies on Metal Derivatives of Buckminsterfullerene (C<sub>60</sub>). *J. Am. Chem. Soc.* **1992**, *114*, 7807–7813.
- (31) Lynn, M. A.; Lichtenberger, D. L. Comparison of the Bonding of Benzene and C<sub>60</sub> to a Metal Cluster: Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6$ ) and Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_{60}$ ). *J. Cluster Sci.* **2000**, *11*, 169–188.
- (32) Babcock, A. J.; Li, J.; Lee, K.; Shapley, J. R. Electrochemistry of Carbidopentaruthenium C<sub>60</sub> Complexes and Related Clusters. *Organometallics* **2002**, *21*, 3940–3946.
- (33) (a) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. Isolation of the Heterofullerene C<sub>59</sub>N as Its Dimer (C<sub>59</sub>N)<sub>2</sub>. *Science* **1995**, *269*, 1554–1556. (b) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. Synthesis and X-ray structure of dumb-bell-shaped C<sub>120</sub>. *Nature* **1997**, *387*, 583–586. (c) Segura, J. L.; Martín, N. [60]Fullerene dimers. *Chem. Soc. Rev.* **2000**, *29*, 13–25.
- (34) Balch, A. L.; Costa, D. A.; Fawcett, R.; Winkler, K. Electronic Communication in Fullerene Dimers. Electrochemical and Electron Paramagnetic Resonance Study of the Reduction of C<sub>120</sub>O. *J. Phys. Chem. B* **1996**, *100*, 4823–4827.
- (35) Dragoe, N.; Shimotani, H.; Hayashi, M.; Saigo, K.; de Bettencourt-Dias, A.; Balch, A. L.; Miyake, Y.; Achiba, Y.; Kitazawa, K. Electronic Interactions in a New Fullerene Dimer: C<sub>122</sub>H<sub>4</sub>, with Two Methylene Bridges. *J. Org. Chem.* **2000**, *65*, 3269–3273.
- (36) Dragoe, N.; Shimotani, H.; Wang, J.; Iwaya, M.; de Bettencourt-Dias, A.; Balch, A. L.; Kitazawa, K. First Unsymmetrical Bisfullerene, C<sub>121</sub>: Evidence for the Presence of Both Homofullerene and Methanofullerene Cages in One Molecule. *J. Am. Chem. Soc.* **2001**, *123*, 1294–1301.

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