

[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 η^2 -C₆₀, μ - η^2 : η^2 -C₆₀, and μ_3 - η^2 : η^2 : η^2 -C₆₀ π -type bonding modes. Multiple C₆₀ 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 C₆₀ ligand between π and σ (μ_3 - η^1 : η^1 : η^2 -C₆₀ and μ_3 - η^1 : η^2 : η^1 -C₆₀) types as well as reversible interconversion between μ_3 - η^2 : η^2 : η^2 -C₆₀ and μ - η^2 : η^2 -C₆₀. The μ_3 - η^2 : η^2 : η^2 -C₆₀ metal cluster complexes show remarkable electrochemical stability and an unusually strong electronic communication between C₆₀ and metal cluster centers.

Introduction

Full-fledged research efforts in C₆₀ science, made possible by the availability of fullerene C₆₀ in mass quantity,¹ have produced numerous fullerene derivatives.^{2,3} In particular, exohedral metallofullerenes have attracted a lot of attention concerning the effects of metal coordination on the chemical and physical properties of C₆₀ as well as with the direct analogy to carbon nanotubes decorated by metal nanoparticles.^{3,4} Prior to our investigations on the interaction between C₆₀ and metal clusters, exohedral

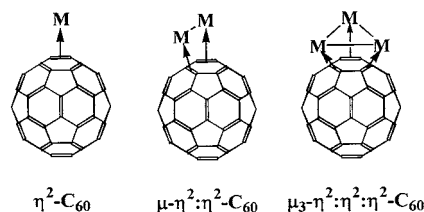
Kwangyeol Lee, born in 1971, received his B.S. degree from KAIST in 1992 and his Ph.D. degree, under the supervision of Prof. John R. Shapley, from University of Illinois at Urbana—Champaign in 1997. Since 1998, he has been working as a postdoctoral associate in Prof. Park's group at KAIST. His research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

Hyunjoon Song, born in 1973, received his B.S. degree in 1994 and his Ph. D. degree in 2000, under the direction of Prof. Joon T. Park from KAIST. He is currently a postdoctoral associate in Prof. Park's group at KAIST, working on the chemistry and application of fullerenes and carbon nanomaterials.

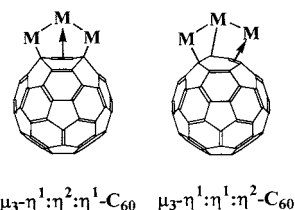
Joon T. Park, born in 1949, received his B.S. in chemistry at Seoul National University in 1972 and M.S. in physical chemistry at KAIST in 1975. He then spent four years at the chemistry division of the Agency for Defense Development (ADD). He came to the United States in 1979, completed his M.S. in 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 C₆₀—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 π -type C₆₀—metal interactions with η^2 -C₆₀ (for most metals)⁵ and μ - η^2 : η^2 -C₆₀ (for bimetallic Re₂, Ru₂, and Ir₂)⁶ bonding modes. Our group and that of Shapley have independently prepared various C₆₀—metal cluster complexes and demonstrated that a variety of cluster frameworks [Re₃(μ -H)₃,⁷ Ru₃,^{8,9} Os₃,^{10–12} Ru₅C,^{13,14} Os₅C,^{15,16} PtRu₅C,¹⁴ Ru₆C,¹³ and Rh₆¹⁷] can bind to C₆₀ via a face-capping cyclohexatriene-like bonding mode, μ_3 - η^2 : η^2 : η^2 -C₆₀. In particular, we have been interested in converting the μ_3 - η^2 : η^2 : η^2 -C₆₀ bonding mode to new ones by modifying the coordination sphere of the metal centers to which C₆₀ is coordinated, and we have unraveled an aspect of C₆₀ as a versatile, multifunctional ligand exhibiting various π - and σ -bonding modes. We also demonstrated an unusually strong electronic communication between C₆₀ 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,³ they fall short of describing the significant advances achieved recently in the area of C₆₀—metal cluster complexes. In this Account, we aim to discuss general synthetic methods, novel bonding modes of the C₆₀ ligand on cluster frameworks, and unique electrochemical properties of C₆₀—metal cluster complexes.

π complex



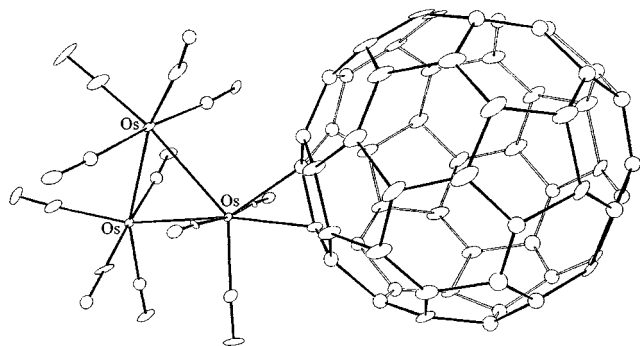
σ - π mixed complex



Synthesis and Structural Characterization of μ_3 - η^2 : η^2 : η^2 -C₆₀ Metal Clusters

[60]Fullerene—metal cluster complexes have been prepared either by direct thermal reaction of the second-row transition metal carbonyl clusters with C₆₀ or by chemical activation of the third-row metal carbonyl clusters with Me₃NO/MeCN followed by reaction with C₆₀.^{7–17} Chlorobenzene is the solvent of choice for the preparation of the C₆₀—metal cluster complexes because it dissolves a large quantity of C₆₀, has a relatively high boiling point that is useful for thermal reactions, and can be easily

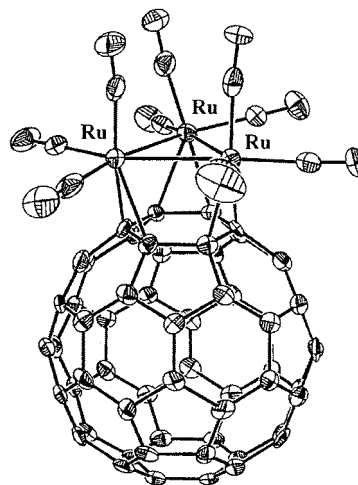
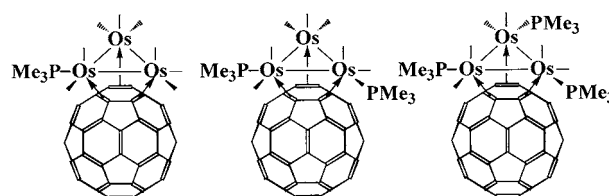
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FIGURE 1. Molecular structure of **1**.

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**),^{18,19} 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 η^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 η^2-C_{60} complexes.⁵ 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 π -backdonation in **1** is significantly suppressed by the presence of strong π -acid carbonyl ligands on the osmium atoms. Longer C–C distances have been observed for other η^2-C_{60} complexes with donor phosphine ligands at the metal center: 1.45 Å in $Pd(PPh_3)_2(\eta^2-C_{60})$,^{5f} 1.48 Å in $RhH(CO)(PPh_3)_2(\eta^2-C_{60})$,^{5g} 1.50 Å in $W(CO)_3(dppe)(\eta^2-C_{60})$,^{5h} and 1.53 Å in $Ir(CO)Cl(PPh_3)_2C_{60}$.^{5b} 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.¹⁰

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%).¹⁰ A better yield (32%) was obtained from an alternative reaction of $Os_3(CO)_{10}(NCMe)_2$ and C_{60} in refluxing chlorobenzene.¹⁰ 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%).⁸ 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- π orbital at an angle (ca. 10°) away from perpendicular to the face of the C_6 -

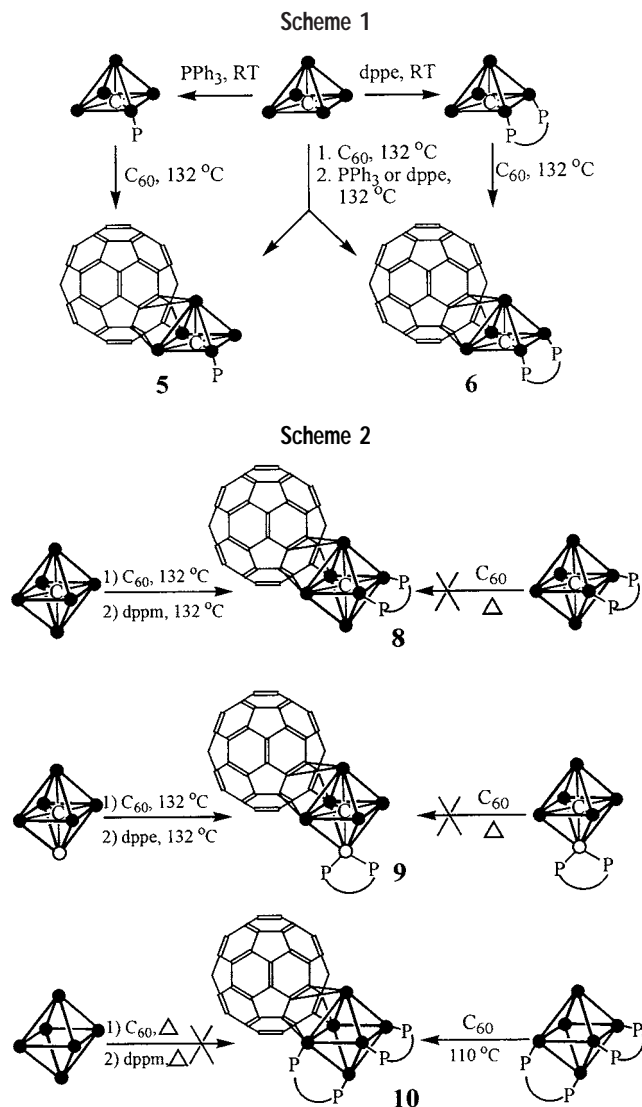
FIGURE 2. Molecular structure of **3**.FIGURE 3. Propeller-like geometry for phosphine substitution in **2**.

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

Homologous complexes **2** and **3** undergo carbonyl substitution reactions with phosphine ligands to afford $M_3(CO)_{9-n}(PPh_3)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$ ($M = Ru, Os; n = 1, 2$)^{9,11} or $M_3(CO)_{9-n}(PMe_3)_n(\mu_3-\eta^2-\eta^2-\eta^2-C_{60})$ ($M = Os; n = 1, 2, 3$)¹² 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 3.¹²

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.⁷ 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.⁷ Interestingly, the phosphine or isocyanide ligand in these compounds takes an axial position on a rhenium atom for both steric and electronic reasons.⁷

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(diphenylphosphino)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).^{13,14} 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 C_{60} . Regardless of the reaction sequence, the ligand substitution reactions are regiospecific. The C_{60} is coordinated to a triangular face of square-pyramidal Ru_5C framework, and the phosphine ligand coordinates the basal ruthenium atom that does not interact with the 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 C_{60} in refluxing chlorobenzene.^{15,16}

Three hexanuclear octahedral cluster frameworks, Ru_6C ,¹³ PtRu_5C ,¹⁴ and Rh_6 ,¹⁷ can interact with 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 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**),¹³ 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 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**).¹⁴ 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 C_{60} .¹⁷ Interestingly, syntheses of hexanuclear C_{60} cluster com-

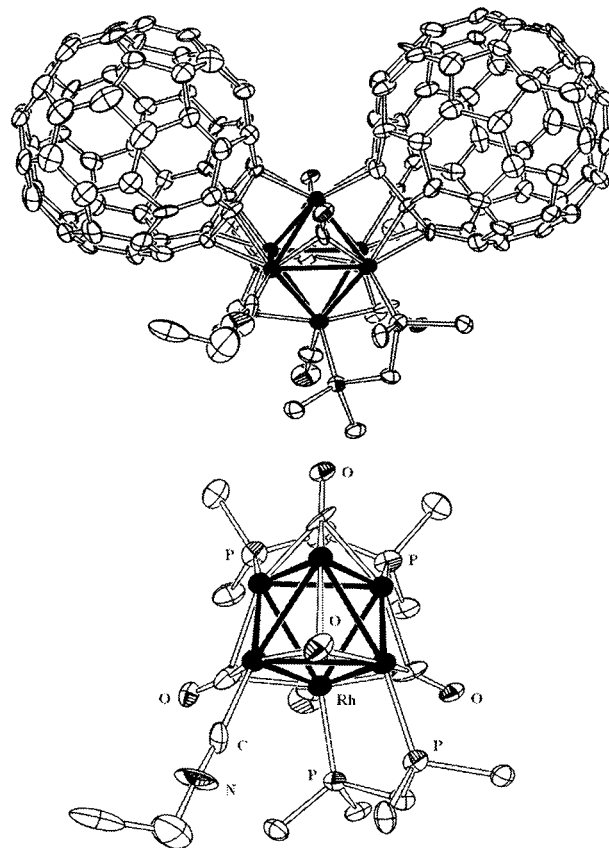
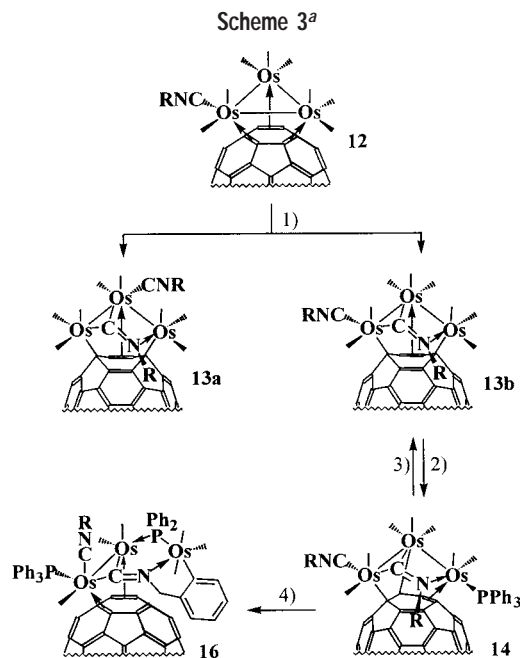


FIGURE 4. Molecular structure of **11**. Phenyl groups except ipso-carbons are removed for clarity.

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

Multiple C_{60} Coordination on a Single Cluster Core. Until recently, multiple coordination of C_{60} to a single metal center had not been accomplished, even though C_{60} , with a cone angle of 120° , 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 C_{60} , can form a stable bisfullerene adduct with a striking feature of a single metal bridging two C_{60} cages.¹⁷ Reaction of **10** with excess 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 C_{60} coordination on a single metal atom.¹⁷ Compound **11** exhibits two face-capping C_{60} ligands on two 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 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 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



^a R = CH₂C₆H₅. Reagents and conditions: (1) RNC, ClC₆H₅, 80 °C; (2) (a) Me₃NO, MeCN/ClC₆H₅, RT, (b) PPh₃, ClC₆H₅, 70 °C; (3) CO (2 atm), ClC₆H₅, 100 °C; (4) PPh₃, ClC₆H₅, 132 °C.

of the first bisfullerene adduct, Tang et al. reported the preparation of monometallic bisfullerene compounds, [M(η²-C₆₀)₂(CO)₂(dbcbipy)] (M = W and Mo, dbcbipy = 4,4'-di(butylcarboxyl)-2,2'-bipyridine), in which two trans C₆₀ ligands bind to a single metal atom in an η² fashion.²²

Ligand-Induced Transformation of C₆₀ Bonding Modes

Interconversion between π and σ Bonding Modes. Reaction of Os₃(CO)₈(CNR)(μ₃-η²:η²:η²-C₆₀) (R = CH₂C₆H₅) (**12**) and CNR at 80 °C in chlorobenzene forms two isomeric σ-π mixed type compounds, Os₃(CO)₈(CNR)(μ₃-CNR)(μ₃-η¹:η²:η¹-C₆₀) (**13a,b**) (Scheme 3).²³ The external CNR ligand inserts into an Os–Os bond to give a bent Os₃ framework and coordinates to the three osmium metal centers via a 4e-donor μ₃-η² 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 C₆₀–metal σ-complex. The two outer osmium atoms coordinate to the C1 and C4 atoms of the C₆₀ ligand in a σ fashion, respectively, while the central osmium atom is π-coordinated to the C2 and C3 atoms in an η² mode. The two Os–C (C₆₀) σ-bonds (2.25 and 2.26 Å) are shorter than the Os–C₂ π-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 sp³-hybridized carbons (328° and 327°) are considerably smaller than those (av. 351°) for the other four carbon atoms with a sp² hybridization. Thus, the two sp³-hybridized carbon atoms (C1 and C4) are pulled away

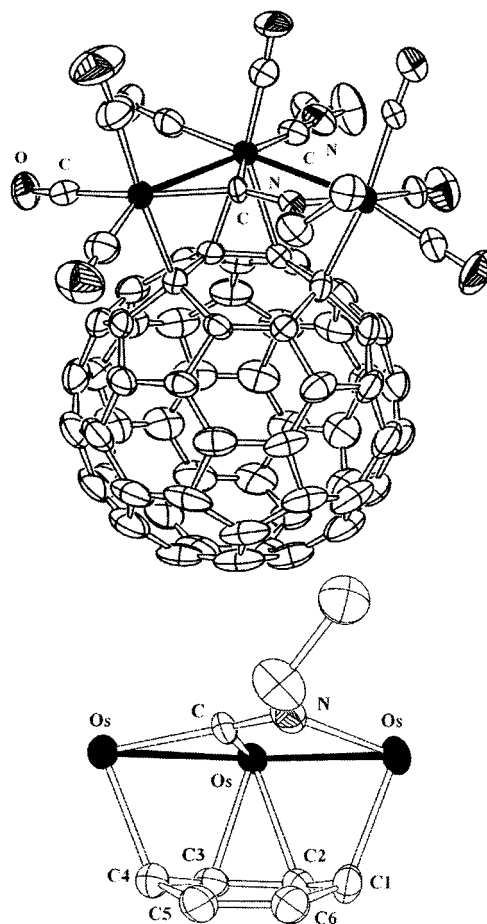


FIGURE 5. Molecular structure of **13a**. Phenyl groups except ipso-carbons are removed for clarity.

from the smooth curvature of the C₆₀ ligand, which is manifested by the boat shape of the C₆-ring, with sp³-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 C₆-ring of C₆₀ 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 π-interactions in **12** to give two Os–C (C₆₀) σ-bonds and an uncoordinated C=C bond in **13a** and **13b**. The 1,4-addition isomer of C₆₀–metal σ-complexes has been proposed previously in a few cases, such as in C₆₀{Re(CO)₅}₂ and C₆₀{Mo(CO)₃(η⁵-C₅H₄CO₂Et)}₂.²⁴

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

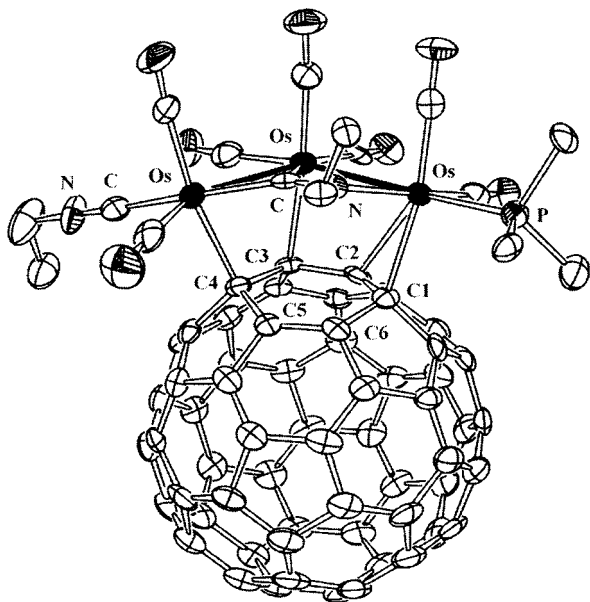


FIGURE 6. Molecular structure of **14**. Phenyl groups except ipso-carbons are removed for clarity.

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 Me₃NO/MeCN and subsequent reaction with PPh₃ produces Os₃(CO)₇(CNR)(μ₃-CNR)(PPh₃)(μ₃-η¹:η¹:η²-C₆₀) (**14**), in which the PPh₃ ligand occupies an equatorial position of a terminal osmium atom by replacing a carbonyl ligand (Figure 6).²⁵ The μ₃-η¹:η²:η¹-C₆₀ (1,4-disubstituted cyclohexadiene-like C₆-ring) moiety in **13b** has undergone further orbital rearrangement to form the μ₃-η¹:η¹:η²-C₆₀ (1,2-disubstituted cyclohexadiene-like C₆-ring) ligand (Scheme 3). The two Os–C (C₆₀) 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 C₆-ring of C₆₀. While the bulky PPh₃ ligand is coordinated at the less hindered outer osmium site, a similar reaction with PMe₃ produces Os₃(CO)₇(CNR)(μ₃-CNR)(PMe₃)(μ₃-η¹:η²:η¹-C₆₀) (**15**), in which the smaller PMe₃ ligand merely substitutes an axial carbonyl ligand on a central osmium atom without changing the C₆₀ bonding mode. The metal center coordinated by the donor phosphine ligand apparently prefers a π-interaction with C₆₀ because of back-donation from the metal to C₆₀. The PPh₃ ligand is easily replaced by CO to result in clean conversion of **14** to **13b**, which represents a reversible interconversion between the μ₃-η¹:η²:η¹-C₆₀ and μ₃-η¹:η¹:η²-C₆₀ bonding modes.

Further interaction of **14** with PPh₃ at an elevated temperature forms a π-type complex, Os₃(CO)₆(CNR)(μ₃-CNCH₂C₆H₄)(PPh₃)(μ-PPh₂)(μ-η²:η²-C₆₀) (**16**), in which the C₆₀ ligand has regained the cyclohexatriene-like C₆-ring hybridization (Scheme 3).²⁵ One Os–Os bond in **14** is ruptured, and the two intact osmium metals are bridged by a μ-η²:η²-C₆₀ ligand. The bridging isocyanide ligand is

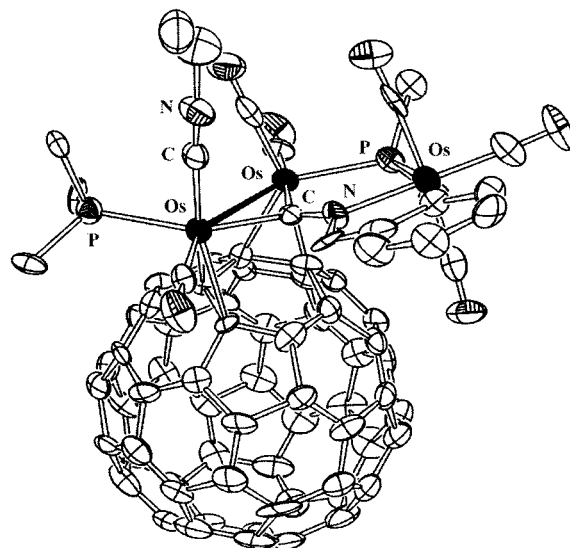
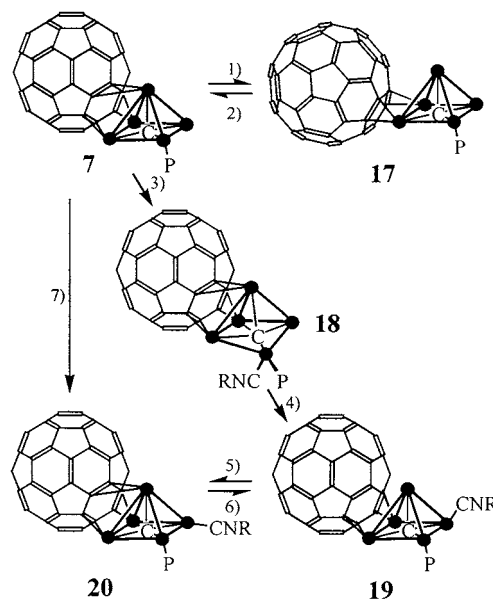


FIGURE 7. Molecular structure of **16**. Phenyl groups except ipso-carbons are removed for clarity.

Scheme 4^a

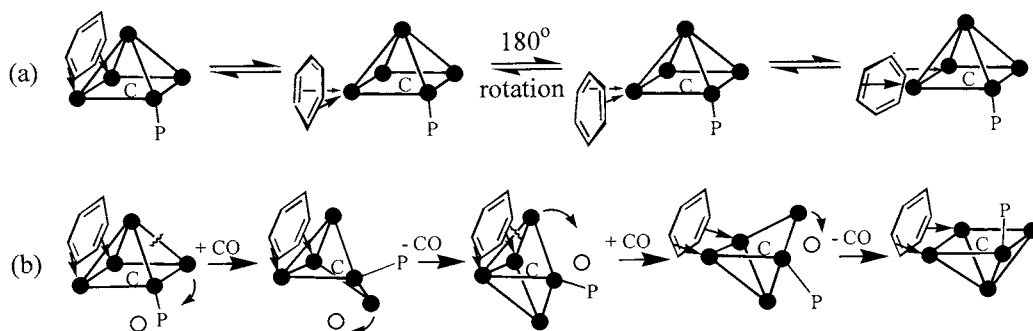


^a R = CH₂C₆H₅, P = PPh₃. Reagents and conditions: (1) CO (1 atm), ClC₆H₅, 80 °C; (2) ClC₆H₅, 132 °C; (3) RNC, ClC₆H₅, RT; (4) ClC₆H₅, 100 °C; (5) Me₃NO, MeCN/ClC₆H₅, RT; (6) ClC₆H₅, 132 °C; (7) CO (3 atm), ClC₆H₅, 55 °C; (8) excess Ph₃P=NCH₂Ph, ClC₆H₅, RT.

bonded to all three Os centers, but the phenyl group orthometalates to the released osmium atom, forming a five-membered metalacycle (OsNC₃), as shown in Figure 7. A benzene molecule, formed by coupling of a hydride from the orthometalation and a phenyl group from PPh₃, is dissociated from the molecule to give the μ-PPh₂ moiety.

Reversible Interconversion between μ-η²:η²-C₆₀ and μ₃-η²:η²:η²-C₆₀. Os₅C(CO)₁₁(PPh₃)(μ₃-η²:η²:η²-C₆₀) (**7**) reacts with CO to form Os₅C(CO)₁₂(PPh₃)(μ-η²:η²-C₆₀) (**17**), in which two adjacent double bonds in a C₆-ring of C₆₀ bridge the two basal osmium atoms (Scheme 4).^{15,16} The third uncoordinated double bond in the C₆-ring of **17** is placed away from the Os₃ triangle; the C₆₀ 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 $(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})[\text{Re}_2\text{H}_8(\text{PMe}_3)_4]$.⁶ Thermolysis of **17** results in loss of a carbonyl ligand, C_{60} rotation by 180° , and re-formation of a $\text{Os}\text{-C}_2$ (C_{60}) bond to give **7**, which demonstrates a reversible interconversion between $\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$ and $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{60}$.^{15,16}

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 $\text{Os}_{\text{apical}}\text{-Os}_{\text{basal}}$ bonds in the square-pyramidal Os_5C framework is cleaved to form a “wing-tip-bridged butterfly” framework.^{15,16} 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 $\text{Os}\text{-Os}$ 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 $\text{Os}_{\text{apical}}\text{-C}_2$ (C_{60}) interaction.^{15,16} In this transformation, the C_{60} rotation does not take place, unlike the interconversion between **7** and **17**. Decarbonylation of **19** with $\text{Me}_3\text{NO}/\text{MeCN}$ 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.¹⁶

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_{60} 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_{60} 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 $\eta^4\text{-cyclohexadiene}$ moiety on a metal center has been well documented for Os_3 cluster compounds.²⁶ The other mechanism, hinted at by the isocyanide ligand addition reaction of **7**, would be a metal framework rearrangement, which involves a series of $\text{Os}\text{-Os}$ bond scissions and formations

to invert the square-pyramidal Os_5C cluster framework (Scheme 5b). In this “octahedral site exchange” mechanism, a carbonyl addition induces an $\text{Os}\text{-Os}$ 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, $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$.²⁷

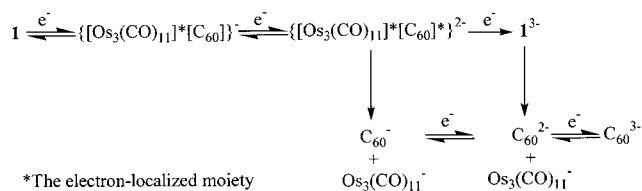
Electrochemical Properties

Free C_{60} is known to be fairly electronegative, being reducible up to C_{60}^{6-} due to its triply degenerate LUMO.²⁸ Electrochemical studies of monometallic C_{60} derivatives such as $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})(\eta^2\text{-C}_{60})$ ²⁹ and $(\text{Et}_3\text{P})_2\text{M}(\eta^2\text{-C}_{60})$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$)³⁰ have revealed C_{60} -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_{60} 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 $E_{1/2} = -1.08\text{ V}$, is slightly more negative than that of free C_{60} , at $E_{1/2} = -1.05\text{ V}$,¹⁹ which is consistent with metal-to- C_{60} π -back-donation, as was shown in other monometallic C_{60} complexes.^{29,30} However, the second and third reductions appear at potentials more positive by 0.10 and 0.29 V, respectively, than those of free C_{60} . This unusual anodic shifts and the IR spectroelectrochemical study of **1** imply that the first electron accepted via the C_{60} ligand in **1** is delocalized to the triosmium center with its strong π -acid carbonyl ligands, as shown in Scheme 6.¹⁹ 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_{60} reveal that a similar C_{60} -mediated electron delocalization occurs in **21**²⁻ and **22**²⁻ 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 C_{60} and Various $\eta^2\text{-C}_{60}$ and $\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60}$ Metal Clusters

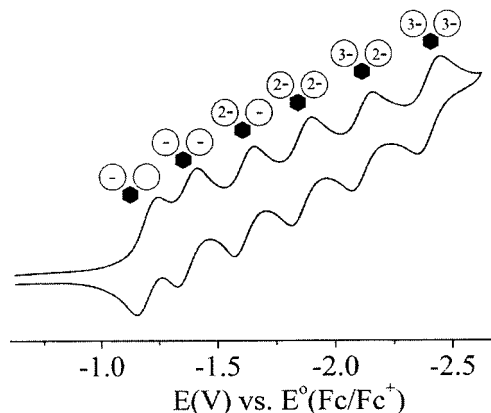
compound	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	$E_{1/2}^{-3/-4}$	solvent	ref
C_{60}	-1.05 (-1.08)	-1.41 (-1.44)	-1.87 (-1.90)		DM/Tol	19
$\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_{60})$ (1)	-1.08 (-1.12)	-1.31 (-1.34)	<i>b</i> (-1.61)		DM/Tol	19
$\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ (21)	-1.16 (-1.18)	-1.44 (-1.49)	<i>b</i> (-1.68)		DM/Tol	19
$\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$ (22)	-1.19 (-1.21)	-1.53 (-1.56)	<i>b</i> (-1.76)		DM/Tol	19
C_{60}	-1.08	-1.46	-1.90	-2.38	DCB	11
$\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$ (2)	-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
C_{60}	-1.06	-1.43	-1.91	-2.38	CB	7
$\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_{60})$ (4)	-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

^a The cathodic peak potentials (E_{pc}) at the scan rate of 20.5 V/s are given in parentheses. ^b 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 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 C_{60} .^{7,11} This anodic shift may be ascribed to the inductive effect of the metal carbonyl cluster adds on the stabilization of the 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.³¹ While the first two reductions place electrons in the mostly 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.³¹ 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 C_{60} complexes, as shown in Table 1. Similar 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.³² This observation promises an important possibility that the electronic properties of 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.³³ In the cases of organic bisfullerene compounds, a weak, through-space electronic communication between C_{60} cages has been observed only for C_{120}O ,³⁴ $\text{C}_{120}(\text{CH}_2)_2$,³⁵ and C_{120}C ,³⁶ 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 C_{60} cages (Figure 8).¹⁷ Each redox wave of **11** corresponds to sequential, pairwise addition of six electrons into the two C_{60} centers to form $\text{C}_{60}^-\text{-Rh}_6\text{-C}_{60}$, $\text{C}_{60}^{2-}\text{-Rh}_6\text{-C}_{60}$, $\text{C}_{60}^{2-}\text{-Rh}_6\text{-C}_{60}^-$, ..., and ultimately $\text{C}_{60}^{3-}\text{-Rh}_6\text{-C}_{60}^{3-}$. The electronic environment for the two C_{60} centers in **11** is very similar despite the difference in coordination spheres around the two C_{60} centers, since there is little difference between donor effects of a phosphine ligand and a benzyl isocyanide ligand in C_{60} -metal cluster complexes.¹⁷ 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 C_{60} ligands reflect an unusually strong electronic communication between the two C_{60} centers via the Rh_6 spacer. In compound **11**, the long distance (3.55 Å) between the two C_{60} centers limits π -orbital overlap of separate 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 C_{60} moieties.

Concluding Remarks

[60]Fullerene can bind a variety of metal clusters via η^2 - C_{60} , μ - η^2 : η^2 - C_{60} , and μ_3 - η^2 : η^2 : η^2 - C_{60} π -type bonding modes, acting as 2e-, 4e-, and 6e-donor ligands. Interestingly, modification of the coordination sphere of μ_3 - η^2 : η^2 : η^2 - C_{60} metal cluster complexes results in new bonding modes, such as π -type μ - η^2 : η^2 - C_{60} and σ - σ mixed types μ_3 - η^1 : η^2 : η^1 - and μ_3 - η^1 : η^1 : η^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 σ -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- π orbitals and metal d- π orbitals in μ_3 - η^2 : η^2 : η^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 Fullerenes. *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 – η -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 μ_3 - η^2 : η^2 : η^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 η^2 - C_{60} and μ_3 - η^2 : η^2 : η^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 μ_3 - η^2 : η^2 : η^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 μ_3 - η^2 : η^2 : η^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 μ - η^2 : η^2 - C_{60} and μ_3 - η^2 : η^2 : η^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 μ - η^2 : η^2 - C_{60} and μ_3 - η^2 : η^2 : η^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. π -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 μ_3 - η^1 : η^2 : η^1 - C_{60} Bonding Mode: Ligand-Induced Conversion of π to σ 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 π to σ C₆₀–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 C₆₀ with Pentacarbonylrhenium Radicals. Reversible Formation of C₆₀{Re(CO)₅}₂. *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 σ -Bonded Fullerene Metal Derivatives from Reactions of Fullerene Dianion C₆₀²⁻ 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 [M₃(CO)₉($\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6$)] 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 [M₃H(CO)₉($\mu_3\text{-}\sigma\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_7$)] (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 C₆₀⁶⁻ and C₇₀⁶⁻: 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 C₆₀-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 (C₆₀). *J. Am. Chem. Soc.* **1992**, *114*, 7807–7813.
- (31) Lynn, M. A.; Lichtenberger, D. L. Comparison of the Bonding of Benzene and C₆₀ to a Metal Cluster: Ru₃(CO)₉($\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6$) and Ru₃(CO)₉($\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_{60}$). *J. Cluster Sci.* **2000**, *11*, 169–188.
- (32) Babcock, A. J.; Li, J.; Lee, K.; Shapley, J. R. Electrochemistry of Carbidopentaruthenium C₆₀ 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 C₅₉N as Its Dimer (C₅₉N)₂. *Science* **1995**, *269*, 1554–1556. (b) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. Synthesis and X-ray structure of dumb-bell-shaped C₁₂₀. *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 C₁₂₀O. *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: C₁₂₂H₄, 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, C₁₂₁: 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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