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Synthesis and Characterization of μ_3-η^2,η^2,η^2-C_{60} Trirhenium Hydrido Cluster Complexes

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The reaction of C_{60} with $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ in refluxing chlorobenzene produces $Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**1**) in 50% yield. Initial decarbonylation of **1** with Me_3NO/MeCN followed by reaction with PPh_3 in boiling chlorobenzene affords $Re_3(\mu\text{-}H)_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**2**) in a low yield (26%). Treatment of **1** with $PhCH_2N{=}PPh_3$ at room temperature gives a benzyl isocyanide substituted product $Re_3(\mu\text{-}H)_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**3**) in 53% yield. Compounds **1**, **2**, and **3** have been isolated as crystalline solids and characterized by spectroscopic (infrared, mass, ^1H, ^{31}P, and ^{13}C NMR) and analytical data. The structure of **3** has been determined by a single-crystal X-ray diffraction study. The C_{60} ligand is coordinated to the trirhenium triangle in a μ_3-η^2,η^2,η^2 bonding mode, and the benzyl isocyanide ligand occupies an axial position of a rhenium atom. Electrochemical properties of **1** and **2** have been studied by cyclic voltammetry (CV) in chlorobenzene (CB) solutions. The general features of CV curves have revealed four reversible redox couples for **1** and **2** in the CB potential window. The CV results suggest that a C_{60}-mediated electron transfer to the trirhenium center takes place in $\mathbf{1}^{2-}$ species for **1** and $\mathbf{2}^{3-}$ for **2**.

Introduction

The interaction between metal clusters and a carbon cluster C_{60} is one of the most interesting topics in the area of exohedral metallofullerene chemistry.[1] In particular, the metal cluster−C_{60} complexes among metallofullerenes can be viewed as molecular analogues of metal and carbon hybrid materials, namely, carbon nanotubes on one hand and metal nanoparticles on the other, which receive much current attention due to their potential for future technological applications.[2] Since our initial report on metal cluster−C_{60} complexes,[3] subsequent development in π-complex chemistry has resulted in η^2-C_{60}, μ-η^2,η^2-C_{60}, and μ_3-η^2,η^2,η^2-C_{60} complexes mainly in group 8 metals such as Os_3,[4] Os_5C,[5] Ru_3,[6] Ru_5C, Ru_6C, and $PtRu_5C$,[7] and the face-capping cyclohexatriene-like bonding mode, μ_3-η^2,η^2,η^2-C_{60}, is a dominant one in these cluster complexes. In our previous work, some of triosmium−C_{60} complexes have revealed an unusual electronic communication between metal cluster and C_{60} centers,[4b,8] which may be useful for the development of specific electronic application in materials science. We have recently demonstrated that the existing C_{60} bonding modes on the cluster framework can be converted to new ones by modifying the coordination sphere of metal centers to which C_{60} is coordinated. The first example of reversible interconversion between μ-η^2,η^2-C_{60} and μ_3-η^2,η^2,η^2-C_{60} has been observed on an Os_5C cluster framework by addition or elimination of 2e-donor ligands such as carbon monoxide and benzyl isocyanide.[5] Our further efforts have resulted in transformation of μ_3-η^2,η^2,η^2-C_{60} to a new σ-type μ_3-η^1,η^2,η^1-C_{60} ligand on a triosmium cluster framework upon insertion of a benzyl isocyanide ligand into an Os−Os bond.[9] As an extension of our work on these metal cluster−C_{60} complexes, we employed as a metal cluster moiety the trirhenium hydridocarbonyl group, $Re_3(\mu\text{-}H)_3(CO)_9$, which is isoelectronic with $Os_3(CO)_9$. Herein we report the synthesis and characterization of a C_{60}−trirhenium hydridocarbonyl complex, $Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**1**), and its substitution products, $Re_3(\mu\text{-}H)_3(CO)_8L(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (L = PPh_3 (**2**); $PhCH_2NC$ (**3**)).

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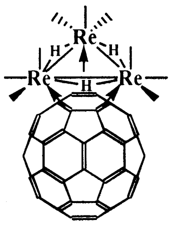

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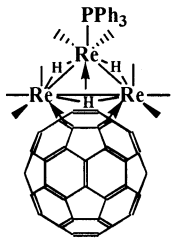

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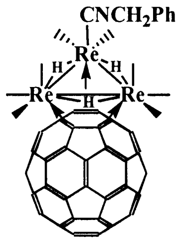

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Results and Discussion

Synthesis and Characterization of 1−3. A chlorobenzene solution of C_{60} and excess (2 equiv) $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ was heated at reflux for 3 h. Evaporation of the solvent and purification by TLC (silica gel, CS_2) afforded $Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**1**) as a red brown solid ($R_f = 0.9$, 50%). Initial decarbonylation of **1** with Me_3NO/MeCN and subsequent reaction with PPh_3 in boiling chlorobenzene gave $Re_3(\mu\text{-}H)_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**2**) as a brown solid (26%), whereas treatment of **1** with $PhCH_2N{=}PPh_3$ at room temperature produced a benzyl isocyanide substituted product, $Re_3(\mu\text{-}H)_3(CO)_8(PhCH_2NC)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**3**), as a red brown solid (53%). Triphenylphosphinalkylimine reagents are known to react with metal carbonyl complexes to yield metal isocyanide substituted compounds.[10] Compounds **1** and **3** are soluble in CS_2 and chlorinated benzenes, but **2** is sparingly soluble in these solvents.

Formulation of the $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60}$ trirhenium hydrido complexes, **1**−**3**, is supported by both elemental analysis and the molecular ion (M^+) multiplet in the FAB positive ion mass spectrum (MS) of each compound. The M^+ multiplet in the MS of **1**−**3** matches perfectly the calculated pattern [the highest peak in the M^+ multiplet (*m*/*z*, found, calcd); **1** (1534, 1534), **2** (1769, 1769), and **3** (1624, 1624)].

The NMR data indicates an idealized C_{3v} symmetry for **1** in solution similar to the previously reported $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$.[4] The $^{13}C\{^1H\}$ NMR spectrum (CO region, 298 K) shows a single resonance at δ 183.2 for the nine carbonyls, which implies the presence of a fast localized 3-fold rotation of three carbonyl groups on each rhenium atom at room temperature. The ^{13}C NMR spectrum of the C_{60} region (see the top spectrum of Figure 1) reveals 12 resonances at δ 152.7, 150.0, 147.6, 146.5, 145.4, 144.7, 144.6, 143.6, 143.3, 142.6, 141.3, and 76.8. The four sp^2 carbon resonances (three carbon atoms each) at δ 150.0, 143.6, 143.3, and 142.6 labeled as "•" appear with about half of the intensity of the other seven sp^2 carbon resonances (six carbon atoms each). The unique high-field signal at δ 76.8 is assigned to an sp^3 carbon resonance (six carbon atoms) directly bonded to the rhenium atoms. This high-field chemical shift is comparable to those of $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (δ 61.2)[4b] and $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (δ 73.3).[6b] The general features of the IR spectrum of **1** are quite similar to those of $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$.[4b]

Both spectroscopic data and structural characterization (vide infra) indicate that compounds **2** and **3** have a C_s symmetric nature, in which the PPh_3 and $PhCH_2NC$ ligands occupy an axial position, respectively. The ^1H NMR spectra of **2** and **3** show two hydridic resonances (**2**; δ −14.5 ($J_{PH} = 15.2$ Hz) and −15.6, **3**; δ −14.8 and −15.3) with an intensity ratio of 2:1, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at δ 8.9. Complex **3** is much more soluble in CS_2 than **2**, and thus ^{13}C NMR spectrum has been obtained for **3**. The $^{13}C\{^1H\}$ NMR spectrum (CO region, 298 K) of **3** exhibits four resonances at δ 189.5, 186.8, 184.3, and 183.6 in a ratio of 2:2:2:2 for the eight carbonyls. The four signals can be assigned to a pair of axial carbonyls and three inequivalent pairs of equatorial carbonyls, which implies no carbonyl fluxionality in **3** in contrast to **1**. The C_s symmetric nature of **3** reveals three sp^3 carbon resonances (δ 82.1, 77.2, and 67.3) and 29 sp^2 carbon resonances comprised of 25 and 4 (δ 150.2, 144.0, 143.7, and 142.7 denoted as •) lines in an intensity ratio of 2:1 (see the bottom spectrum of Figure 1). The IR spectra (CO region) of **2** and **3** are similar to each other, but are different from that of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, in which the phosphine ligand occupies an equatorial site.[4b]

The axial preference of PPh_3 and $PhCH_2NC$ ligands in **2** and **3** could be explained by both steric and electronic reasons. Equatorial sites at each rhenium center are sterically very conjested with six coordination, and intramolecular axial interaction is diminished by the lengthening of the Re−Re bonds due to the bridging hydrides (vide infra).[11] Donor ligands such as PPh_3 and $PhCH_2NC$ coordinated *trans* to a hydride ligand (equatorial site) are electronically disfavored with respect to those *trans*s to an electron-withdrawing C_{60} ligand (axial site).[12]

Crystal Structure of 3·CS₂. The overall molecular geometry and the atomic labeling scheme of **3** are illustrated in Figure 2. Interatomic distances and angles are listed in Tables 1 and 2, respectively. Compound **3** has a triangle of rhenium atoms, with the three edges bridged by hydride ligands. All the rhenium atoms bear four terminally bonded (CO, $PhCH_2NC$, and C_{60}) 2e-donor ligands, so that the coordination around each rhenium atom is nearly octahedral. It has an idealized C_s symmetry, with a mirror plane containing the Re(1) atom and bisecting the Re(2)−Re(2)′ bond. A benzyl isocyanide ligand is coordinated to the Re(1) atom in an axial position and lies in the mirror plane. The axial isocyanide ligand and two axial carbonyls are parallel with respect to the normal vector of the Re_3 plane. However, in other structurally characterized Ru_3 and Os_3 complexes, such as $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[6a] $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[4b] $Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[4c] and $Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[4c] carbonyl and phosphine ligands on each metal center are slightly twisted all in the same direction and the three axial carbonyls are disposed in a propeller-like configuration. This structural difference is likely to be ascribed to the elongated Re−H−Re bonds (av 3.189(1) Å) due to the hydride ligands,[11] which compares with Ru−Ru (av 2.88(1) Å for $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[6a] and Os−Os (av 2.917 (1) Å for $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$[4b]) bond lengths. The angle between equatorial carbonyls (av

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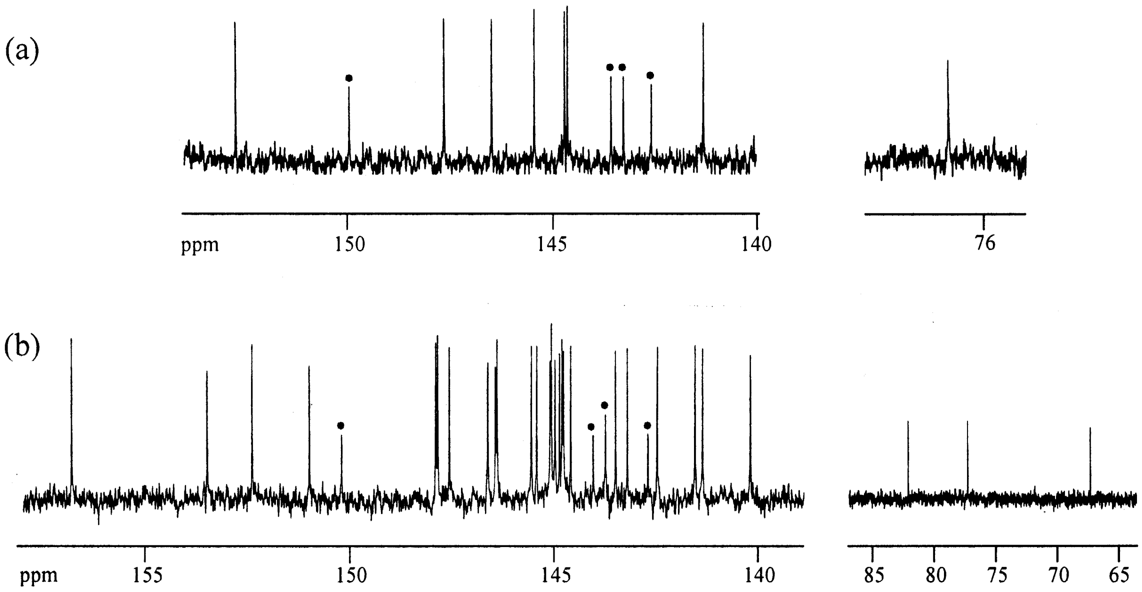

Figure 1. ^{13}C NMR spectrum (C_{60} region, 100 MHz) of **1** (a) and **3** (b).

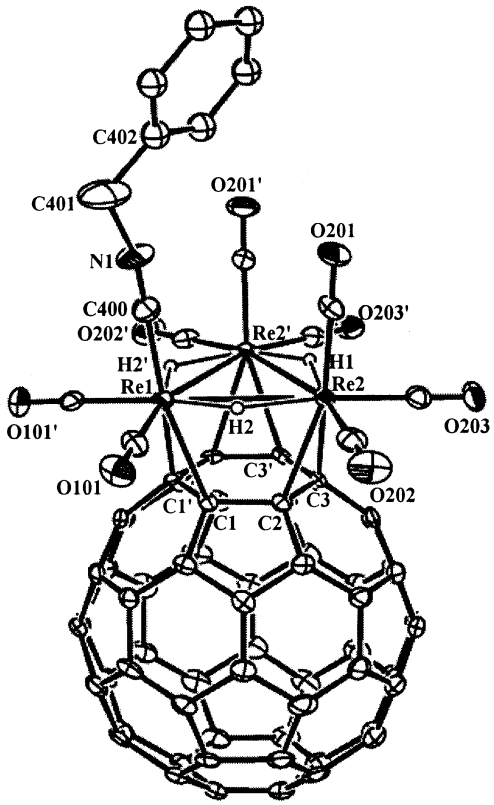

Figure 2. Molecular geometry and atomic labeling scheme for **3**. Solvate molecule and disordered atoms are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Esd's for 3·CS_2

(A) Metal−Metal Distances			
Re(1)−Re(2)	3.1858(8)	Re(2)−Re(2)′	3.194(1)
(B) Metal−Carbon (Carbonyl and Isocyanide) Distances			
Re(1)−C(101)	1.94(2)	Re(2)−C(201)	1.95(2)
Re(2)−C(202)	1.91(2)	Re(2)−C(203)	1.94(2)
Re(1)−C(400)	2.00(2)		
(C) Carbon−Nitrogen and Carbon−Oxygen Distances			
C(101)−O(101)	1.13(2)	C(201)−O(201)	1.13(2)
C(202)−O(202)	1.18(2)	C(203)−O(203)	1.14(2)
C(400)−N(1)	1.16(3)		
(D) Metal−Hydride Distances			
Re(1)−H(2)	1.7(1)	Re(2)−H(1)	1.71(7)
Re(2)−H(2)	1.9(1)		
(E) Metal−Carbon (C_{60}) Distances			
Re(1)−C(1)	2.27(1)	Re(2)−C(2)	2.33(1)
Re(2)−C(3)	2.32(1)		
(F) Distances within the C_{60} Ligand			
C(1)−C(1)′	1.49(3)	C(1)−C(2)	1.48(2)
C(2)−C(3)	1.44(2)	C(3)−C(3)′	1.49(2)
(G) Distances within the Isocyanide Ligand			
C(400)−N(1)	1.16(3)	N(1)−C(401)	1.51(3)
C(401)−C(402)	1.54(4)		

∠C−Re−C = 88.7(8)°) is smaller than those for $Os_3(CO)_8(PPh_3)(\mu_3$-η^2,η^2,η^2-$C_{60})$ (av 95.6°), indicating that equatorial sites in compound **3** are more conjested than those of group 8 metal complexes because of the steric effect of the hydride ligands. The average Re−H bond distance (1.8(1) Å) is comparable with that for $Re_3(\mu$-$H)_3(CO)_{11}(PPh_3)$ (1.822(8) Å).[13]

The C_{60} ligand is coordinated to the Re_3 triangle in a μ_3-η^2,η^2,η^2-C_{60} fashion. A six-membered carbon ring (C_6 ring) of the C_{60} ligand positions centrally over the Re_3 framework (Re(1)−C(1) = 2.27(1) Å, Re(2)−C(2) = 2.33(1) Å, and Re(2)−C(3) = 2.34(1) Å). The C_{60} ring is essentially parallel with the Re_3 plane with a dihedral angle of 1.3° [cf. 0.9° for $Ru_3(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$,[6a] 1.2° for $Os_3(CO)_8(PPh_3)(\mu_3$-η^2,η^2,η^2-$C_{60})$,[4b] and 1.3° for $Os_3(CO)_7(PMe_3)_2(\mu_3$-$\eta^2,\eta^2,\eta^2$-$C_{60})$[4c]]. The C_6 ring is pulled away from the C_{60} surface, consistent with the change in the hybridization to sp^3. The average angle between the metal-coordinated C−C bond vector at the 6,6 ring junction and the plane defined by one of the two carbon atoms and its two neighboring sp^2 and sp^3 carbon atoms is 35(1)°, which is larger than the free C_{60} value of 31°.[14]

All other features of the molecular geometry are within the expected range. The average C−C bond

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Table 2. Selected Interatomic Angles (deg) and Esd's for 3·CS_2

(A) Intermetallic Angles			
Re(2)−Re(1)−Re(2)′	60.17(2)	Re(1)−Re(2)−Re(2)′	59.92(1)
(B) M−M−CO and M−M−CN Angles			
Re(2)−Re(1)−C(101)	103.9(5)	Re(2)′−Re(1)−C(1A)	163.1(5)
Re(1)−Re(2)−C(201)	94.9(4)	Re(1)−Re(2)−C(202)	106.3(5)
Re(1)−Re(2)−C(203)	164.2(4)	Re(2)′−Re(2)−C(201)	95.2(4)
Re(2)′−Re(2)−C(202)	165.0(5)	Re(2)′−Re(2)−C(203)	105.5(4)
Re(2)−Re(1)−C(400)	97.4(5)		
(C) Re−C−O, Re−C−C, and C−Re−C Angles			
Re(1)−C(101)−O(101)	179(1)	Re(2)−C(201)−O(201)	178(1)
Re(2)−C(202)−O(202)	178(1)	Re(2)−C(203)−O(203)	178(1)
Re(1)−C(400)−N(1)	179(2)	C(101)−Re(1)−C(400)	89.9(6)
C(101)−Re(1)−C(101)′	91.2(9)	C(201)−Re(2)−C(202)	91.7(6)
C(202)−Re(2)−C(203)	87.5(7)	C(201)−Re(2)−C(203)	92.3(6)
(D) Angles Involving Metal-Coordinated Carbon in C_{60}			
C(1)′−C(1)−C(2)	119.4(7)	C(1)−C(2)−C(3)	121(1)
C(2)−C(3)−C(3)′	120.0(6)		

length at the junction of the 5,6 ring is 1.45(2) Å, and that at the junction of the 6,6 ring is 1.39(2) Å. The Os−CO distances range from 1.91(2) to 1.95(2) Å, C−O bond lengths range from 1.13(2) to 1.18(2) Å, and Os−C−O angles are in the range 178(1)−179(1)°. The CS_2 solvate molecules do not enter into any significant interactions with molecule **3**.

Electrochemical Studies of 1 and 2. Electrochemical properties of **1** and **2** have been examined by cyclic voltammetry in chlorobenzene (CB) solutions with tetrabutylammonium perchlorate as the supporting electrolyte. Cyclic voltammograms (CV) of **1** and **2** are shown in Figure 3. Half-wave potentials ($E_{1/2}$) of free C_{60}, **1**, **2**, and known triosmium μ_3-η^2,η^2,η^2-C_{60} complexes are summarized in Table 3. The general features of CV curves recorded for **1** and **2** reveal four reversible redox couples for **1** and three redox couples for **2** within the solvent cutoff. The third redox wave of **2** corresponds to a two-electron process, while it could be resolved into two one-electron redox couples at half-wave potentials of −1.75 and −1.77 V by simulation as indicated in Table 3.

The first and second reduction waves of **1** are shifted to more positive potential by ca. 110 and 190 mV, respectively, in comparison with those of free C_{60}. These positive potential shifts by the metal cluster addend on C_{60} have been previously observed in triosmium μ_3-η^2,η^2,η^2-C_{60} complexes as shown in Table 3. The third reduction potential (−1.34 V) of **1** is very close to the second reduction potential (−1.24 V) and even more positive than the second reduction of C_{60} (−1.43 V). This unusually large anodic shift implies that two electrons accepted through the C_{60} ligand in $\mathbf{1}^{2-}$ are significantly delocalized to the trirhenium center. Dianionic species $\mathbf{1}^{2-}$ with electron delocalization to the metal center, therefore, undergoes much easier reduction via the C_{60} ligand than free $C_{60}{}^{2-}$ to afford $\mathbf{1}^{3-}$. This electron delocalization is also reflected in the fourth reduction of **1** with an anodic shift. The direct metal center reduction of $Re_3(\mu\text{-}H)_3(CO)_{12}$ has been observed at far more negative potential of −2.17 V under similar conditions.

The first and second reductions of **2** take place at more negative potentials than those of **1** by 90 and 110 mV, respectively, revealing the electron-donating nature of the phosphine ligand. These values are consistent with the negative shifts (ca. 85 mV) observed in the phosphine-substituted triosmium μ_3-η^2,η^2,η^2-C_{60} complexes.[4b] The first through third reduction potentials of **2** are comparable to those of free C_{60} with anodic shifts, which indicates that three successive C_{60}-localized reductions occur to produce $\mathbf{2}^{-}$, $\mathbf{2}^{2-}$, and $\mathbf{2}^{3-}$. The third and fourth reductions of **2**, however, take place at very close potentials. This observation also supports the conclusion that the electron density in $\mathbf{2}^{3-}$ is significantly delocalized to the trirhenium center, resulting in a large positive shift of the fourth reduction potential of **2**.

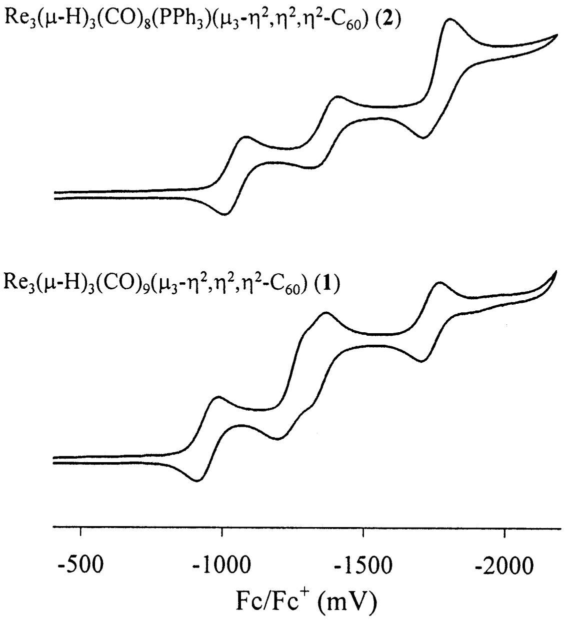

Figure 3. Cyclic voltammograms of **1** and **2** in dry deoxygenated chlorobenzene (0.1 M [(n-Bu)$_4$N][ClO$_4$]). Scan rate = 5 mV/s.

The general electrochemical properties of **1** and **2** are analogous to those of $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**4**) and $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**5**), respectively.[4b] The electron delocalization takes place in $\mathbf{1}^{2-}$ species for **1** and $\mathbf{2}^{3-}$ for **2**. The donor effect of the substituted phosphine ligand results in more negative reduction potentials and significantly affects the electrochemical pathways in these C_{60}−metal cluster complexes. The C_{60}-mediated electronic communication between C_{60} and metal cluster centers has been clearly observed in these C_{60}−trirhenium cluster complexes as well and seems to be a unique general property of C_{60}−metal cluster complexes compared to monometallic C_{60} complexes (e.g., $[(Et_3P)_2M]_n(\eta^2\text{-}C_{60})$ (M = Ni, Pd, Pt; n = 1−4),[15a] $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$,[15b] and $Co(NO)(PPh_3)_2(\eta^2\text{-}C_{60})$[15c]), which showed only C_{60}-localized sequential reductions. Trirhenium centers display a more facile electronic communication with C_{60} than triosmium centers in electronic communication between C_{60} and metal cluster moieties based on the observed reduction potentials ($E_{1/2}{}^{-2/-3}$ = −1.34 (**1**) vs −1.61 (**4**) and $E_{1/2}{}^{-3/-4}$ = −1.77 (**2**) vs −1.95 (**5**)) in Table 3. The μ_3-η^2,η^2,η^2-C_{60} metal cluster complexes have shown a remarkable electro-

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[15] (a) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807. (b) Koefod, R. S.; Xu, C.; Lu, W.; Shapley, J. R.; Hill, M. G.; Mann, K. R. *J. Phys. Chem.* **1992**, *96*, 2928. (c) Chernega, A. N.; Green, M. L. H.; Haggitt, J.; Stephens, H. H. *J. Chem. Soc., Dalton Trans.* **1998**, 755.

Table 3. Half-Wave Potentials ($E_{1/2}$ vs E°_{Fc/Fc^+}) of C_{60}, 1, 2, and Triosmium μ_3-η^2,η^2,η^2-C_{60} Complexes

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}	−1.06	−1.43	−1.91	−2.38	CB	this work
1	−0.95	−1.24	−1.34	−1.73	CB	this work
2	−1.04	−1.35	−1.75	−1.77	CB	this work
C_{60}	−1.08	−1.46	−1.90	−2.38	DCB	4b
$Os_3(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$ (**4**)	−0.98	−1.33	−1.61	−1.74	DCB	4b
$Os_3(CO)_8(PMe_3)(\mu_3$-η^2,η^2,η^2-$C_{60})$ (**5**)	−1.06	−1.42	−1.93	−1.95	DCB	4b

chemical stability, which will be promising in the future technological applications as electronic materials.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried appropriately before use. C_{60} (99.5%, Southern Chemical Group) and triphenylphosphine (99%, Aldrich) were used without further purification. Anhydrous trimethylamine *N*-oxide (mp 225−230 °C) was obtained from $Me_3NO{\cdot}2H_2O$ (98%, Aldrich) by sublimation (3 times) at 90−100 °C under vacuum. $Re_3(\mu$-$H)_3(CO)_{11}(NCMe)$[16] and $PhCH_2N{=}PPh_3$[17] were prepared according to the literature methods. Preparative thin-layer chromatography (TLC) plates were prepared with silica gel GF_{254} (type 60, E. Merck).

Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. Positive ion FAB mass spectra (FAB^+) were obtained by the staff of the Korea Basic Science Center, and all *m*/*z* values were referenced to ^{192}Os. Elemental analyses were provided by the staff of the Energy and Environment Research Center at KAIST.

Preparation of $Re_3(\mu$-$H)_3(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$ (1). A chlorobenzene solution (60 mL) of $Re_3(\mu$-$H)_3(CO)_{11}(NCMe)$ (2 equiv, 151.7 mg, 0.167 mmol) and C_{60} (1 equiv, 60.0 mg, 0.0833 mmol) was heated at reflux for 3 h. Evaporation of the solvent and purification by preparative TLC (CS_2) produced compound **1** (63.3 mg, 0.0413 mmol, 50%, $R_f = 0.9$) as a red-brown solid: IR (CS_2) ν(CO) 2074 (s), 2048 (s), 2008 (m), 1987 (m), 1927 (m) cm^{-1}; ^1H NMR (400 MHz, CS_2/ext. CD_2Cl_2, 298 K) δ −15.1 (s); $^{13}C\{^1H\}$ NMR (100 MHz, CS_2/ext. CD_2Cl_2, 298 K) δ 183.2 (s, 9CO), 152.7 (6C), 150.0 (3C), 147.6 (6C), 146.5 (6C), 145.4 (6C), 144.7 (6C), 144.6 (6C), 143.6 (3C), 143.3 (3C), 142.6 (3C), 141.3 (6C), 76.8 (6C, C_{60} sp^3 carbon); MS (FAB^+) *m*/*z* 1536 (M^+). Anal. Calcd for $C_{69}H_3O_9Re_3$: C, 54.0; H, 0.20. Found: C, 54.1; H, 0.48.

Preparation of $Re_3(\mu$-$H)_3(CO)_8(PPh_3)(\mu_3$-η^2,η^2,η^2-$C_{60})$ (2). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.5 mg, 0.020 mmol) was added dropwise to a chlorobenzene solution (20 mL) of compound **1** (30 mg, 0.0196 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature for 30 min. After evaporation of the solvent in vacuo, the residue was dissolved in chlorobenzene (20 mL) containing PPh_3 (15.3 mg, 0.0583 mmol). The resulting solution was heated at reflux for 90 min. Evaporation of the solvent and purification by TLC (CS_2) gave compound **2** (9.2 mg, 0.0052 mmol, 26%, $R_f = 0.6$) as a brown solid: IR (CS_2) ν(CO) 2059 (vs), 2041 (s), 1995 (sh), 1989 (s), 1977 (m), 1961 (m), 1923 (m) cm^{-1}; ^1H NMR (400 MHz, CS_2/ext. CD_2Cl_2, 298 K) δ 8.1−7.8 (m, 15H), −14.5 (d, $J_{PH} = 15.2$ Hz, 2H), −15.6 (s, 1H); $^{31}P\{^1H\}$ NMR (162 MHz, CS_2/ext. CD_2Cl_2, 298 K) δ 8.9 (s); MS (FAB^+) *m*/*z* 1770 (M^+). Anal. Calcd for $C_{86}H_{18}O_8PRe_3$: C, 58.4; H, 1.03. Found: C, 58.5; H, 1.06.

Preparation of $Re_3(\mu$-$H)_3(CO)_8(PhCH_2NC)(\mu_3$-$\eta^2,\eta^2,\eta^2$-$C_{60})$ (3). A chlorobenzene solution (20 mL) of **1** (30.0 mg, 0.0196 mmol) and $Ph_3P{=}NCH_2Ph$ (14.4 mg, 0.0392 mmol) was stirred at room temperature for 3.5 h. Evaporation of the solvent and separation by TLC (CS_2) afforded compound **3** (16.7 mg, 0.0103 mmol, 53%, $R_f = 0.5$) as a red brown solid: IR (cyclohexane) ν(NC) 2178 (m); ν(CO) 2060 (vs), 2043 (s), 2011 (s), 1986 (m), 1971 (s), 1954 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.6−7.3 (m, 5H), 5.3 (s, 2H), −14.8 (s, 2H), −15.3 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, CS_2/ext. CD_2Cl_2, 298 K) δ 189.5 (2CO), 186.8 (2CO), 184.3 (2CO), 183.6 (2CO), 156.8 (2C), 153.5 (2C), 152.4 (2C), 151.0 (2C), 150.2 (1C), 147.9 (2C), 147.9 (2C), 147.6 (2C), 146.6 (2C), 146.4 (2C), 146.4 (2C), 145.6 (2C), 145.4 (2C), 145.1 (2C), 145.1 (2C), 145.0 (2C), 144.9 (2C), 144.8 (2C), 144.8 (2C), 144.6 (2C), 144.0 (1C), 143.7 (1C), 143.5 (2C), 143.2 (2C), 142.7 (1C), 142.5 (2C), 141.5 (2C), 141.4 (2C), 140.2 (2C), 132.0 (1C, N*C*), 130.5 (2C, phenyl), 130.3 (2C, phenyl), 128.2 (2C, phenyl), 82.1 (2C, C_{60} sp^3), 77.2 (2C, C_{60} sp^3), 67.3 (2C, C_{60} sp^3), 49.7 (1C, Ph*C*H_2); MS (FAB^+) *m*/*z* 1625 (M^+). Anal. Calcd for $C_{76}H_{10}NO_8Re_3$: C, 56.2; H, 0.62; N, 0.86. Found: C, 56.0; H, 0.64; N, 0.90.

Table 4. Crystal and Structure Determination Data for $3{\cdot}CS_2$

formula	$C_{76}H_{10}NO_8Re_3{\bullet}CS_2$
fw	1623.54
system	orthorhombic
space group	*Pnma*
a, Å	19.405(2)
b, Å	13.163(1)
c, Å	20.044(2)
V, $Å^3$	5119.8(7)
Z	4
D_{calcd}, Mg m^{-3}	2.205
temp, K	233(2)
λ(Mo Kα), Å	0.71073
μ, mm^{-1}	7.230
θ range for collection	$1.85° \le \theta \le 23.28°$
index ranges	$-21 \le h \le 21$, $-14 \le k \le 14$, $-22 \le l \le 22$
no. of rflns measd	31 107
no. of unique rflns	3882
no. of rflns ($I > 2\sigma(I)$)	3299
R_f[a]	0.0526
R_w[b]	0.1524
GOF	1.033

[a] $R_f = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Electrochemical Measurements. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.) electrochemical analyzer using the conventional three-electrode system of a platinum working electrode (1.6 mm diameter disk, Bioanalytical Systems, Inc.), a platinum counter wire electrode (5 cm length of 0.5 mm diameter wire), and a Ag/Ag^+ reference electrode (0.1 M $AgNO_3$/Ag in acetonitrile with a Vycor salt bridge). All measurements were performed at ambient temperature under nitrogen atmosphere in a dry deoxygenated 0.1 M chlorobenzene solution of $[(n\text{-}Bu)_4N][ClO_4]$. The concentrations of compounds were ca. 3×10^{-4} M. All potentials were referenced to the standard ferrocene/ferrocenium (Fc/Fc^+) scale.

X-ray Structure Determination for $3{\cdot}CS_2$. Crystals of **3** suitable for an X-ray diffraction study were grown by slow diffusion of hexane into a carbon disulfide solution of **3** at room temperature. A brownish black crystal of **3** (0.62 × 0.14 × 0.12 mm) was mounted on a Simens SMART diffractometer/CCD area detector. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. Each series consisted of 15 frames collected at intervals of 0.3° ω scan with the exposure time of

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[16] Bruce, M. I.; Low, P. J. *J. Organomet. Chem.* **1996**, *519*, 221.

[17] Lee, K.-W.; Singer, L. A. *J. Org. Chem.* **1974**, *39*, 3780.

10 s per frame. A total of 31 107 reflections collected at 233 K were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Details of relevent crystallographic data are summarized in Table 4.

The structure of **3** was solved by direct and different Fourier methods and was refined by the full-matrix least-squares methods based on F^2. The crystallographic mirror plane passed through Re(1) and the midpoint of the Re(2)−Re(2)′ bond so that four atoms of the isocyanide ligand, four atoms of the C_{60} ligand, and one bridging hydride atom were located on the mirror plane. Five carbon atoms of the benzyl isocyanide ligand were disordered in two orientations (see Supporting Information), with their positions and thermal parameters fixed due to high thermal motions. Other non-hydrogen atoms were refined with anisotropic thermal coefficients. Three bridging hydrogen atoms were directly located from the E-map and refined isotropically. For all computations the SHELX97 package was used, and the function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/[\sigma^2(F_o{}^2) + (0.1123P)^2]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.[18] The number of parameters refined was 405, and the final reliability factors for 3882 unique reflections ($I > 2\sigma(I)$) were R1 = 5.26%, wR2 = 15.24% ($(\Delta/\sigma)_{max} = 0.000$, $\Delta\rho_{max}/\Delta\rho_{min} = 2.575/-3.771$ e Å^{-3} in final $\Delta\rho$ map), and GOF = 1.033.

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Supporting Information Available: A figure of disordered geometry for complex **3** with a complete atomic labeling scheme, and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and complete bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0101341

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[18] Sheldrick, G. M. *SHELX97*, Program for Crystal Structure Refinement; University of Göettingen: Germany, 1997.