Syntheses, Structures, and Electrochemical Properties of $Os_3(CO)_{9-n}(CNCH_2Ph)_n(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ ($n = 2-4$)

Chang Yeon Lee,[†] Bo Keun Park,[†] Jung Hee Yoon,[‡] Chang Seop Hong,[‡] and
Joon T. Park*,[†]

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, and Department of Chemistry and Center for Electro- and Photo-Responsive Molecules, Korea University, Seoul, 136-701, Korea

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Benzyl isocyanide-substituted C_{60}-triosmium complexes, $Os_3(CO)_{9-n}(CNCH_2Ph)_n(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (n = 2 (**3**), 3 (**4**), and 4 (**5**)), have been prepared by reactions of either $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) or its lesser isocyanide-substituted complexes with appropriate amounts of (triphenylphosphino)benzylimine ($PhCH_2N{=}PPh_3$). Compounds **3**−**5** have been characterized by spectroscopic (IR, MS, ^1H and ^{13}C NMR) methods, cyclic voltammetry, and X-ray diffraction studies. Single-crystal X-ray diffraction studies reveal that isomer **3a** has two inequivalent equatorial isocyanide ligands as a *cis,trans*-1,2-isomer and isomer **4a** has three equivalent equatorial isocyanide ligands as a 1,2,3-isomer with C_3 symmetry. In compound **5**, one benzyl isocyanide is axially coordinated to an osmium atom, whereas the other three benzyl isocyanide ligands are equatorially coordinated to each osmium atom. ^1H and ^{13}C NMR data, however, indicate that compound **3** exists as a mixture of 1,2- (**3a**) and 1,1-isomers (**3b**) in a ratio of 7:1, compound **4** as a mixture of 1,2,3- (**4a**) and 1,1,2-isomers (**4b**) in a ratio of 1:1, and compound **5**, interestingly, as a single species of a 1,1,2,3-isomer in solution. The cyclic voltammetric studies reveal that all the CVs of **3**−**5** and related $Os_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**) show four reversible redox waves that correspond to a one-electron process each with the third and fourth waves overlapped within the chlorobenzene solvent potential window. As more isocyanide ligands are coordinated in **2**−**5**, all the corresponding half-wave potentials are gradually shifted to more negative potentials, reflecting the electron-donor property of the isocyanide ligand. Furthermore, C_{60}-mediated electron delocalization from C_{60} to the triosmium center takes place in the trianionic species of **2**−**5**. The two isomers of **3** and **4** apparently undergo an equivalent electrochemical process, respectively.

Introduction

The interaction between metal clusters and a carbon cluster such as [60]fullerene (C_{60}) is one of the most interesting topics in the area of exohedral metallofullerene chemistry.[1] In particular, we have been interested in C_{60}−metal cluster complexes in order to investigate and understand the effects of metal cluster coordination on the chemical and physical properties of C_{60} and the reactivities and electrochemical properties of these complexes[2a] and ultimately to develop new electronic nanomaterials and nanodevices.[2b] The C_{60}−metal cluster complexes have been dominated by a π-type C_{60}−metal cluster interaction with the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ bonding mode. This unique π-bonding nature in C_{60}−metal cluster complexes, surprisingly, results in both remarkable thermal stability and strong electronic communication between C_{60} and metal cluster centers.[2a] Furthermore, this electronic communication can be fine-tuned with various ligands of different electronic properties coordinated on the metal cluster center.[2a] We have also demonstrated that the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ bonding mode can be modified by altering the coordination sphere of the metal centers to which C_{60} is coordinated.[4c,d,6,9] This has led to continued and vigorous studies of C_{60}−metal cluster chemistry, in which ligand substitution controls the fullerene tuning in terms of electrochemical properties and reactivities. This substitution chemistry is important in stabilizing

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* Corresponding author. E-mail: joontpark@kaist.ac.kr. Fax: + 82-42-869-5826.

[†] KAIST.

[‡] Korea University.

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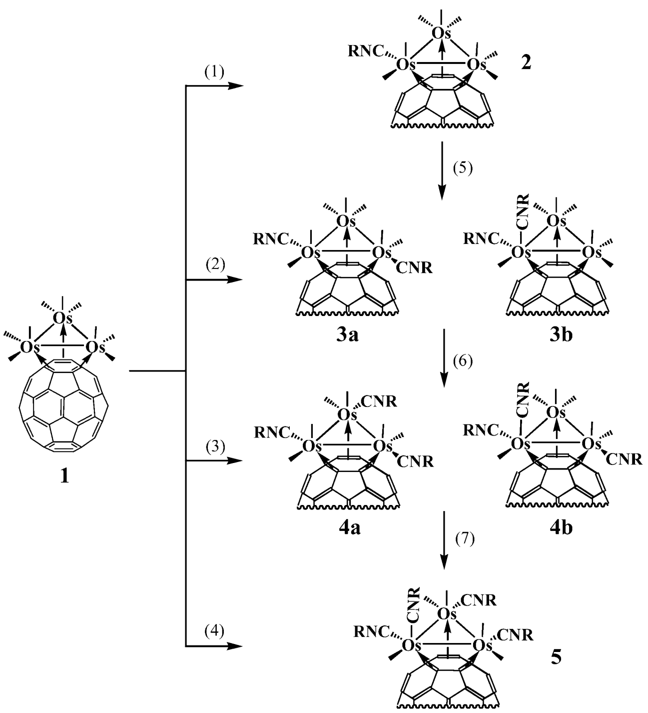
Scheme 1[a]



[a] Legend: (1) 1.2 equiv of RN═PPh$_3$, room temperature, 12 h, 76%; (2) 3 equiv of RN═PPh$_3$, room temperature, 12 h, 70%; (3) 5 equiv of RNdPPh$_3$, 120 °C, 3 h, 70%; (4) 10 equiv of RN═PPh$_3$, 132 °C, 3 h, 40%; (5) 1.5 equiv of RN═PPh$_3$, room temperature, 12 h, 70%; (6) 1.2 equiv of RN═PPh$_3$, 120 °C, 3 h, 70%; (7) 5 equiv of RN═PPh$_3$, 132 °C, 3 h, 28%. R = CH$_2$Ph.

a great variety of C_{60}−metal cluster complexes, which should facilitate the future nanotechnological applications employing these complexes. In our previous work, various phosphine ligand substitution chemistry has been intensively investigated in [$Re_3(\mu\text{-}H)_3$],[3] [Os_3],[4] [Ru_5C],[5] [Os_5C],[6] [Ir_4],[7] and [Rh_6][8] cluster systems to establish the general trend of the reactivity and electrochemical properties of these complexes.

We have previously reported that the reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) with (triphenylphosphino)benzylimine (PhCH$_2$N═PPh$_3$) produces a benzyl isocyanide-substituted product, $Os_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**),[9] in which the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ ligand transforms into a new $\sigma-\pi$ mixed type $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60}$ ligand by insertion of a benzyl isocyanide ligand into an Os−Os bond. An isolobal rhenium analogue, $Re_3(\mu\text{-}H)_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$,[3] has the benzyl isocyanide ligand occupying an axial site, and there is a unique electrochemical effect of the isocyanide ligand in the trirhenium system. Furthermore, the benzyl isocyanide ligand has been successfully employed to significantly increase solubility of a bisfullerene hexarhodium cluster complex, $Rh_6(CO)_5(dppm)_2(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})_2$,[8] which otherwise could not be characterized. As an extension of our ongoing efforts, we herein report the synthesis, structures, and electrochemistry of a variety of benzyl isocyanide-substituted C_{60}-triosmium complexes, $Os_3(CO)_{9-n}(CNCH_2Ph)_n(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (n = 2 (**3**), 3 (**4**), and 4 (**5**)), from reactions of either $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) or its lesser isocyanide-substituted complexes with appropriate amounts of PhCH$_2$N═PPh$_3$ and varying reaction time and temperature, as shown in Scheme 1.

Results and Discussion

Syntheses of 3−5. Synthetic procedures for **2**−**5** are summarized in Scheme 1. The synthesis and structure of compound **2** have already been reported in our earlier account.[9] Compound **3** was prepared in 70% yield from the reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) with 3 equiv of PhCH$_2$N═PPh$_3$ in chlorobenzene (CB) at room temperature for 12 h. Compound **3** can be alternatively prepared from the reaction of **2** with 1.5 equiv of PhCH$_2$N═PPh$_3$ in CB at room temperature for 12 h in a similar yield. Thermolysis of **1** with 5 equiv of PhCH$_2$N═PPh$_3$ in CB at 120 °C for 3 h afforded compound **4** in 70% yield, which can also be prepared alternatively from that of **3** with 1.2 equiv of PhCH$_2$N═PPh$_3$ in CB at 120 °C for 3 h in a similar yield. Compound **5** was prepared in 40% yield along with formation of **4** (25%) from the reaction of **1** with an excess amount (10 equiv) of PhCH$_2$N═PPh$_3$ in refluxing CB for 3 h, whereas thermal reaction of **4** with 5 equiv of PhCH$_2$N═PPh$_3$ in CB at 120 °C for 3 h produces compound **5** in low yield (28%). All the yields for the formation of **3**−**5** were optimized in this study. The substitution with the benzyl isocyanide ligand is also possible by initial decarbonylation of the corresponding starting materials with Me$_3$NO/MeCN reagent for the preparation of **2**−**5**, but the solid (triphenylphosphino)benzylimine reagent is convenient to handle and usually gives better yields without the unpleasant smell of the isocyanide reagent.

Table 1. Selected Interatomic Distances (Å) and esd's for 3a, 4a, and 5

	3a	**4a**	**5**
Os(1)−Os(2)	2.8871(7)	2.907(1)	2.8880(6)
Os(2)−Os(3)	2.9016(7)	2.903(1)	2.9189(6)
Os(1)−Os(3)	2.9270(8)	2.889(1)	2.8951(7)
Os(1)−C(100)	1.98(2)	1.97(2)	1.93(1)
Os(1)−C(110)			1.98(1)
Os(2)−C(200)	2.00(2)	1.97(2)	2.00(1)
Os(3)−C(300)		1.93(2)	1.98(1)
Os(1)−C(1)	2.22(1)	2.23(1)	2.23(1)
Os(1)−C(2)	2.27(1)	2.30(1)	2.29(1)
Os(2)−C(3)	2.25(1)	2.28(1)	2.22(1)
Os(2)−C(4)	2.23(1)	2.27(1)	2.29(1)
Os(3)−C(5)	2.22(1)	2.24(1)	2.21(1)
Os(3)−C(6)	2.28(1)	2.29(1)	2.27(1)
C(1)−C(2)	1.44(2)	1.47(2)	1.43(1)
C(2)−C(3)	1.47(2)	1.48(2)	1.49(2)
C(3)−C(4)	1.42(2)	1.41(2)	1.47(2)
C(4)−C(5)	1.49(2)	1.51(2)	1.48(1)
C(5)−C(6)	1.43(2)	1.42(2)	1.46(2)
C(6)−C(1)	1.47(2)	1.50(2)	1.47(2)
C(100)−N(1)	1.13(2)	1.14(2)	
C(200)−N(2)	1.11(2)	1.14(2)	
C(300)−N(3)		1.12(2)	
C(100)−N(100)			1.19(2)
C(110)−N(110)			1.14(2)
C(200)−N(200)			1.15(2)
C(300)−N(300)			1.18(2)

X-ray Crystal Structures of 3a, 4a, and 5. The overall molecular geometry and the atomic labeling schemes of **3a**, **4a**, and **5** are illustrated in Figures 6, 7, and 8, respectively. Their structures are presented in Scheme 1. Selected interatomic distances and angles of the three compounds are listed in Tables 1 and 2, respectively.

The overall structural features of **3a** are similar to those of isomorphous *cis,trans*-$Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$.[4b] Two inequivalent benzyl isocyanide ligands adopt the less sterically hindered equatorial positions at the two adjacent osmium atoms in a *cis* and *trans* configuration with respect to the Os1−Os2 edge. The two $Os(CO)_2(CNCH_2Ph)$ and one $Os(CO)_3$ unit are twisted slightly, all in the same direction, so that the three axial carbonyls are disposed in a propeller-like configuration. Compound **4a** has three equatorial benzyl isocyanide ligands, which are arranged as far from the other two as possible with a pseudo-C_3 symmetry, as reported in $Os_3(CO)_6(PMe_3)_3$-

Table 2. Selected Interatomic Angles (deg) and esd's for 3a, 4a, and 5

	3a	4a	5
Os(2)−Os(1)−Os(3)	59.869(19)	60.13(2)	60.627(16)
Os(1)−Os(2)−Os(3)	60.748(18)	59.63(2)	59.806(16)
Os(2)−Os(1)−C(100)	149.6(5)	144.8(5)	145.9(5)
Os(3)−Os(1)−C(100)	90.9(5)	84.9(5)	85.9(5)
Os(1)−Os(2)−C(200)	91.7(5)	80.7(5)	165.3(3)
Os(3)−Os(2)−C(200)	152.4(5)	139.9(5)	130.5(3)
Os(2)−Os(3)−C(300)		94.2(6)	84.6(4)
Os(1)−Os(3)−C(300)		154.2(6)	143.1(4)
Os(2)−Os(1)−C(110)			85.7(4)
C(2)−C(1)−C(6)	119.4(11)	116.6(10)	120.5(10)
C(1)−C(2)−C(3)	120.4(11)	120.0(11)	120.7(9)
C(2)−C(3)−C(4)	119.3(10)	122.3(12)	118.8(9)
C(3)−C(4)−C(5)	121.4(11)	118.8(11)	119.8(9)
C(4)−C(5)−C(6)	118.7(11)	119.4(11)	120.3(10)
C(5)−C(6)−C(1)	120.6(11)	122.6(11)	119.9(9)
Os(1)−C(100)−N(1)	174.2(18)	176.3(18)	
Os(2)−C(200)−N(2)	175.3(15)	177.0(15)	
Os(3)−C(300)−N(3)		176.2(18)	
Os(1)−C(100)−N(100)			176.2(13)
Os(1)−C(110)−N(110)			177.1(12)
Os(2)−C(200)−N(200)			175.5(11)
Os(3)−C(300)−N(300)			176.7(11)

(μ_3-η^2:η^2:η^2-C_{60}).[4b] In compound **5**, a benzyl isocyanide ligand is coordinated on the Os1 atom in the axial position, whereas the other three benzyl isocyanide ligands are equatorially bonded to the Os1, Os2, and Os3 centers, respectively. The equatorially bonded benzyl isocyanide on the Os1 atom is *cis* and *trans* to that on the Os3 atom with respect to the Os1−Os3 edge and *trans* and *trans* to that on the Os2 atom with respect to the Os1−Os2 edge. The two equatorial benzyl isocyanide ligands on the Os2 and Os3 centers are, however, unusually *cis* and *cis* with respect to the Os2−Os3 edge, which seems to be possible because of the relatively long and slim shape of the benzyl isocyanide ligand. The bonding nature between the triosmium framework and C_{60} in the starting material, $Os_3(CO)_9$(μ_3-η^2:η^2:η^2-C_{60}) (**1**), is retained during the formation of **3a**, **4a**, and **5**. All other geometric features are within the expected ranges. The average Os−Os bond lengths of **3a**−**5** (2.9052(7) Å for **3a**, 2.900(1) Å for **4a**, and 2.9001(6) Å for **5**) are slightly elongated compared to that for $Os_3(CO)_{12}$ (2.877(3) Å), presumably due to bulky ligands in **3a**−**5**. The C_6 ring of the C_{60} moiety is parallel with the Os_3 plane in **3a**−**5** (dihedral angles: 0.4° for **3a**, 0.5° for **4a**, and 0.6° for **5**). The Os−CO distances range from 1.88(2) to 1.96(2) Å for **3a**, from 1.86(2) to 1.91(2) Å for **4a**, and from 1.87(1) to 1.91(1) Å for **5**. The C−O bond lengths lie between 1.09(2) and 1.16(2) Å for **3a** (av 1.13(2) Å), 1.13(2) and 1.18(2) Å for **4a** (av 1.16(2) Å), and 1.12(2) and 1.17(2) Å for **5** (av 1.15(2) Å). The average Os−$CNCH_2Ph$ bond distances in **3a**, **4a**, and **5** are 1.99(2), 1.96(2), and 1.97(1) Å, respectively. The average C−N bond lengths in **3a**, **4a**, and **5** are 1.12(2), 1.13(2), and 1.16(2) Å, respectively.

Characterization of 3−5. The new compounds **3**−**5** are soluble in various solvents such as CS_2, dichloromethane, toluene, and chlorinated benzenes: the benzyl isocyanide ligand generally increases solubility of these complexes compared to their carbonyl and phosphine derivatives. All the compounds were formulated on the basis of the molecular ion isotope patterns (*m*/*z* (highest peak): 1722 (**3**); 1811 (**4**); 1900 (**5**)) in the positive ion FAB mass spectra and the microanalytical data.

The IR spectra of **3**−**5** exhibit terminal NC stretching bands in the range 2183−2165 cm^{-1} with intensities increasing as **5** > **4** > **3** (see Figure S2 in the Supporting Information). The terminal CO stretching bands appear in the typical range of 2047−1950 cm^{-1} and shift to the low-energy region by ca. 20 cm^{-1}/ligand as more benzyl isocyanide ligands are coordinated, reflecting the stronger electron-donor effect of the isocyanide ligand relative to the carbonyl ligand.

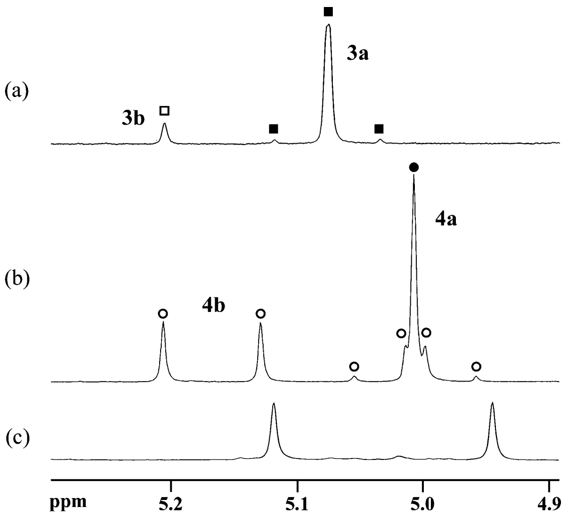


Figure 1. ^1H NMR spectra (400 MHz, $CDCl_3$, 298 K, benzylic region) of (a) **3**, (b) **4**, and (c) **5**.

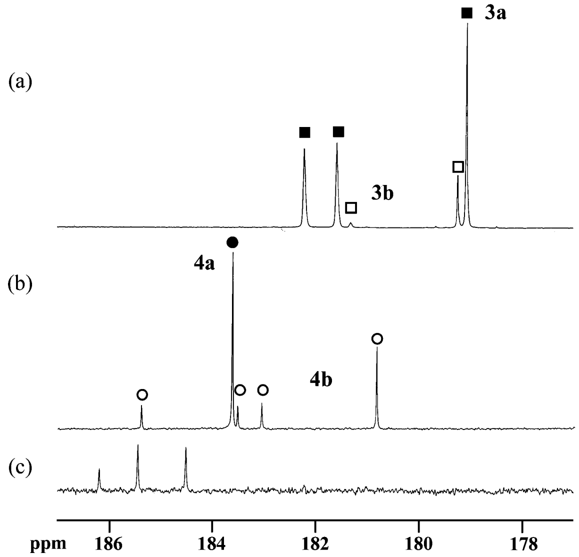
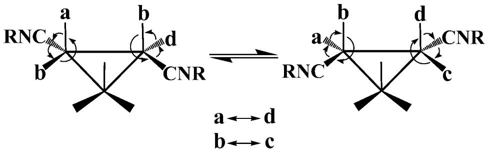


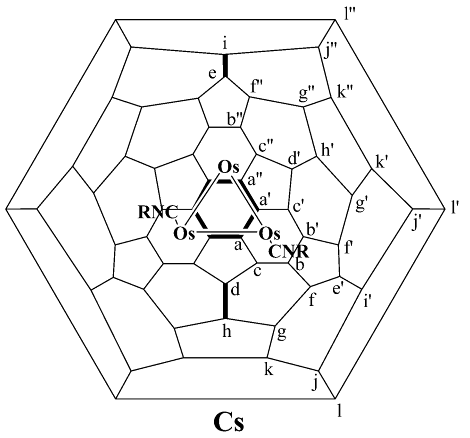
Figure 2. (a) ^{13}CO-enriched ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, carbonyl region) of **3**. (b) ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, carbonyl region) of **4**. (c) ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, carbonyl region) of **5**.

The ^1H and ^{13}C NMR spectra of complexes **3**−**5** at room temperature are shown in Figures 1 and 2, respectively. Both NMR data of **3** appear as two sets of resonances in an intensity ratio of 7:1, implying that **3** exists as two isomers in solution. The ^1H NMR spectrum of **3** (Figure 1a) at room temperature reveals an overlapped AB pattern at δ 5.08 (J_{HH} = 16.4 Hz, denoted as ■) for **3a** and a small singlet at δ 5.21 (denoted as □) for **3b**, for the benzylic protons of the two benzyl isocyanide ligands, respectively. The overlapped AB pattern is ascribed to the diastereotopic benzylic protons of **3a**. The ^{13}C NMR spectrum (carbonyl region, Figure 2a) of ^{13}CO-enriched **3** shows three major resonances at δ 182.2, 181.6, and 179.1 in an intensity ratio of 2:2:3 (denoted as ■) for **3a** and two minor resonances at δ 181.3 and 179.3 in an intensity ratio of 1:6 (denoted as □) for **3b**. The major isomer is identified as an eq,eq-1,2-isomer (**3a**), which is observed in the solid state. The two low-field singlet resonances at δ 182.2 and 181.6 with an equal intensity are due to the equilibration of an axial carbonyl on one osmium center with an equatorial carbonyl on the other

Scheme 2



Scheme 3



2 carbons : a, a', a'' (3)

2 carbons : b, b', b'', c, c', c'', f, f', f'', g, g', g'', j, j', j'', d', e', h', i', k, k', k'', l, l', l'' (25)

1 carbon : d, e, i, h (4)

on the two $Os(CO)_2(CNCH_2Ph)$ moieties due to the well-established coupled restricted 3-fold rotations of the ligands on the two osmium moieties,[4b,10] as presented in Scheme 2. The high-field singlet resonance at δ 179.1 with an intensity 3 is attributed to the three equivalent carbonyls by a fast 3-fold rotation on the $Os(CO)_3$ center. Consequently, the two benzyl isocyanide ligands in **3a** become equivalent: one AB pattern (δ 5.08) and one benzyl isocyanide carbon signal (δ 132.2 (2C, N*C*) and 48.9 (2C, *C*H_2)) appear in the ^1H and ^{13}C NMR spectra, respectively. Isomorphous structures with similar fluxional processes have been previously reported in *cis,trans*-$Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$[10] and *cis,trans*-$Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**7**).[4b] The minor signals are attributed to the ax,eq-1,1-isomer (**3b**), as shown in Scheme 1. The small ^1H NMR resonance at δ 5.21 is due to the proton signals of the two equivalent isocyanide ligands based on the 3-fold rotation of the $Os(CO)(CNCH_2Ph)_2$ center. The two ^{13}C NMR signals at δ 181.3 and 179.3 in an intensity ratio of 1:6 are assigned to one carbonyl on the $Os(CO)(CNCH_2Ph)_2$ center and the other six carbonyls due to fast 3-fold rotations on the two $Os(CO)_3$ centers, respectively. The variable-temperature (VT) ^{13}C NMR spectra of **3** ($CS_2 + CD_2Cl_2$ as an internal reference, see Figure S2 in the Supporting Information) reveal that the resonance at δ 179.3 due to **3b** with an intensity of 6 becomes broad and is finally resolved into two signals (δ 180.3 and 178.3) at 183 K. This observation is consistent with the proposed ax,eq-structure for **3b**, where the two $Os(CO)_3$ centers become equivalent in the high-temperature limiting spectrum. The other possible structure of **3b** with eq,eq-configuration is eliminated, because the signal at δ 179.3 would remain sharp at low temperatures due to a C_s symmetric nature of **3b** that undergoes fast 3-fold rotations of the two $Os(CO)_3$ centers. The ^{13}C NMR (C_{60} region) spectrum of **3a** at room temperature shows 32 resonances (see Scheme 3), as shown in Figure 3, which is consistent with the idealized C_s symmetric nature of **3a** in solution. The spectrum contains 29 sp^2 resonances (δ 158.2−142.4 in Figure 3a) comprising 25 and 4 (δ 152.3, 143.7, 143.0 (1C + 2C, overlapped), and 142.8, denoted as ●) lines in an intensity ratio of 2:1 and three sp^3 carbon resonances of a−a″ (δ 64.1, 62.3, and 54.9 in Figure 3b) with an intensity of 2. The C_{60} carbon resonances of **3b** are too weak to be clearly observed.

The NMR data of **4** also appear as two sets of resonances of **4a** and **4b** in an intensity ratio of 1:1. The ^1H NMR spectrum of **4** (Figure 1b) exhibits a large singlet at δ 5.01 (denoted as ●) for **4a** and two singlets at δ 5.21 and 5.13 and an AB pattern at δ 5.00 ($J_{HH} = 16.4$ Hz) in a ratio of 1:1:1 (denoted as ○) for **4b**, because of the benzylic protons of the three benzyl isocyanide ligands, respectively. These data indicate that **4a** has three equivalent isocyanide ligands and **4b** contains three inequivalent isocyanide ligands. The ^{13}C NMR spectrum (carbonyl region, Figure 2b) of **4** reveals a large resonance at δ 183.7 (denoted as ●) for **4a** and four small resonances at δ 185.4, 183.5, 183.1, and 180.9 in an intensity ratio of 1:1:1:3 (denoted as ○) for **4b**. On the basis of these NMR data, the former resonances are assigned to an eq,eq,eq-1,2,3-isomer (**4a**) with C_3 symmetry observed in the solid state, in which all three isocyanide ligands are equivalent and three axial and three equatorial carbonyl ligands become equivalent by a 3-fold rotation on each osmium center. The large resonance at δ 183.7, therefore, is assigned to the six carbonyl ligands on the three $Os(CO)_2(CNCH_2Ph)$ centers of **4a**. A similar structure that undergoes fluxional processes identical to **4a** was previously reported for $Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$,[4b] which, yet, exists as a single eq,eq,eq-1,2,3-isomer. The other resonances for **4b** are consistent with the structure of an ax,eq,eq-1,1,2-isomer (**4b**), as shown in Scheme 1. Three resonances at δ 185.4, 183.5, and 183.1 each with an intensity of 1 are due to a carbonyl on the $Os(CO)(CNCH_2Ph)_2$ moiety and two inequivalent carbonyls on the $Os(CO)_2(CNCH_2Ph)$ center, although definitive assignments cannot be made. The other resonance at δ 180.9 with an intensity of 3 is due to three carbonyls on the $Os(CO)_3$ center, which undergoes a fast 3-fold rotation at room temperature. Accordingly, three distinct resonances (δ 133.0 (1C, N*C*), 133.0 (1C, N*C*), 132.5 (1C, N*C*); 48.9 (1C, *C*H_2), 48.7 (1C, *C*H_2), and 48.6 (1C, *C*H_2)) are observed for the three inequivalent benzyl isocyanide ligands of **4b**. The ^{13}C NMR spectrum (C_{60} region) of **4a** reveals 12 resonances at δ 159.1 (6C), 153.2 (3C), 148.2 (6C), 146.1 (6C), 145.4 (6C), 144.5 (6C), 144.0 (3C), 143.9 (6C), 143.1 (6C), 143.0 (3C), and 142.6 (3C) for sp^2 carbon atoms (Figure 4a) and 61.0 (6C) for sp^3 carbon atoms (Figure 4b). The four resonances at δ 153.2, 144.0, 143.0, and 142.6 (denoted as ● in Figure 4a) appear with about half of the intensity of the other eight resonances. This observation is consistent with an idealized C_{3v} symmetry of **4a** in solution at room temperature, which contains 12 types of carbon atoms of the C_{60} moiety, i.e., three carbon atoms each for d, e, h, and i types (bold lines) and six carbon atoms each for a, b, c, f, g, k, j, and l types, as analyzed in Scheme 4. The six carbon atoms (a, bold line, sp^3 carbon) coordinated to the osmium atoms appear at δ 61.0 as a singlet (Figure 4b). The small peaks observed in Figure 4a are due to 54 C_{60} sp^2 carbon atoms of **4b**, but six resonances for six inequivalent C_{60} sp^3 carbon atoms are clearly observed at δ 69.7, 66.3, 60.6, 59.6, 55.8, and 51.5 (denoted as ○) in Figure 4b.

The ^1H NMR spectrum of **5** (Figure 1c) shows two singlets at δ 4.94 and 5.12 for the benzylic protons of the four isocyanide ligands in an intensity ratio of 1:1, indicating that the four isocyanide ligands are equivalent pairwise. The ^{13}C NMR

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(10) Hsu, H.-F.; Shapley, J. R. *J. Organomet. Chem.* **2000**, *599*, 97−105.

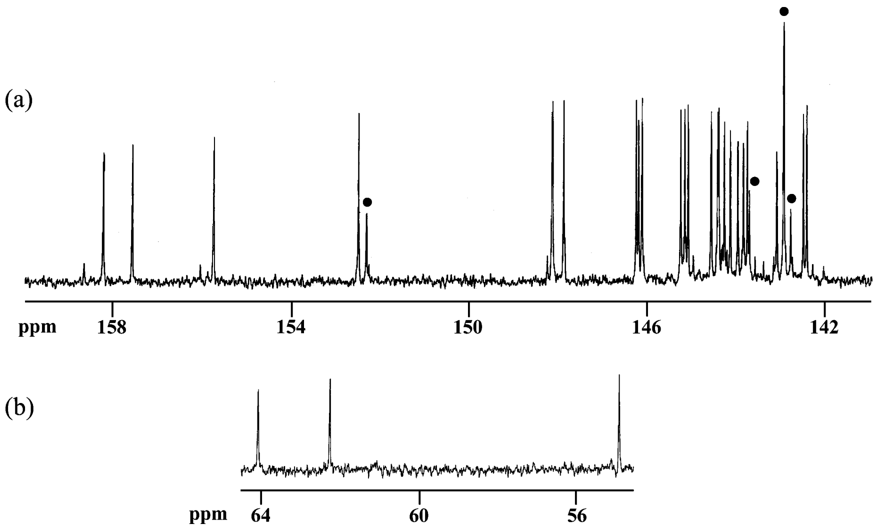


Figure 3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, C_{60} region) of **3**.

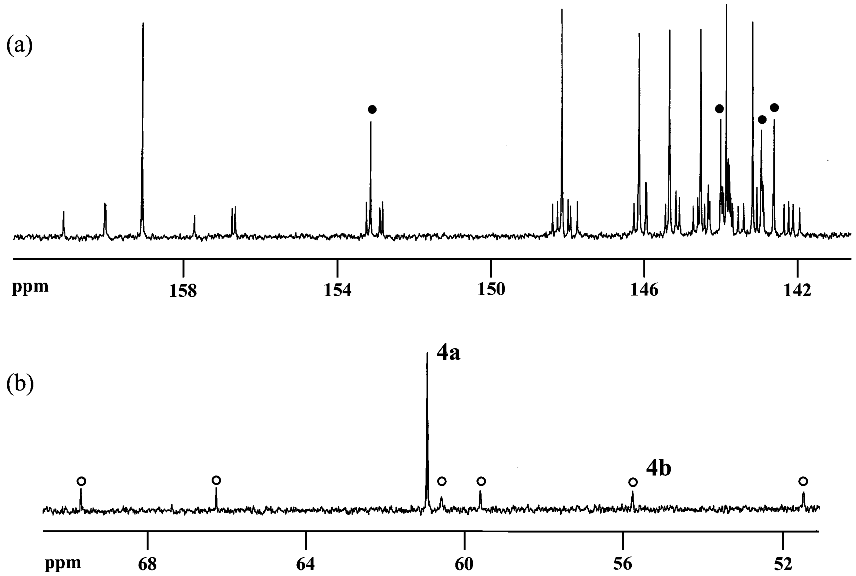
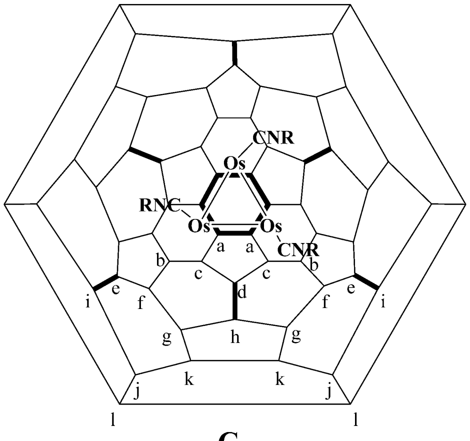


Figure 4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, C_{60} region) of **4**.

Scheme 4



C_{3v}

3 carbons : d, e, h, i (4)

6 carbons : a, b, c, f, g, k, j, l (8)

spectrum (carbonyl region, Figure 2c) of **5** reveals three resonances at δ 186.2, 185.4, and 184.5 in an intensity ratio of 1:2:2. Both NMR data imply that compound **5**, interestingly, exists as a single isomer of ax,eq,eq,eq-1,1,2,3-configuration in solution, as shown in Scheme 1, adopting the structure found in the solid state. The low-field resonance at δ 186.2 with an intensity of 1 is obviously assigned to a carbonyl ligand on the $Os(CO)(CNCH_2Ph)_2$ center and the other two high-field resonances at δ 185.4 and 184.5 each with an intensity of 2 to two axial and two equatorial carbonyls on the two $Os(CO)_2(CNCH_2Ph)$ centers. These NMR data indicate that only the unique $Os(CO)(CNCH_2Ph)_2$ center undergoes a fast 3-fold rotation, leading to a C_s symmetry of this molecule at room temperature. As a result, two types of resonances each with an intensity of 2 due to benzyl isocyanide ligands are also observed in the ^{13}C NMR spectrum (δ 133.5 (2C, N*C*), 133.0 (2C, N*C*); 48.7 (2C, CH_2), 48.5 (2C, CH_2)). The ^{13}C NMR spectrum (C_{60} region) is consistent with a C_s symmetric nature of **5**, as illustrated for compound **3a** in Scheme 2, which comprises 29 sp^2 carbon resonances in the region of δ 162.5−142.6 (sp^2 carbon resonances (d, e, h, and i) are denoted as ● in Figure 5a) and three sp^3 carbon resonances at δ 67.4, 60.2, and 57.9 (Figure 5b).

The carbonyl resonances, apparently, shift to lower fields as the number of benzyl isocyanide ligands on the metal atoms increases, as clearly seen in **3a** (δ 182.2 and 181.6), **3b** (δ

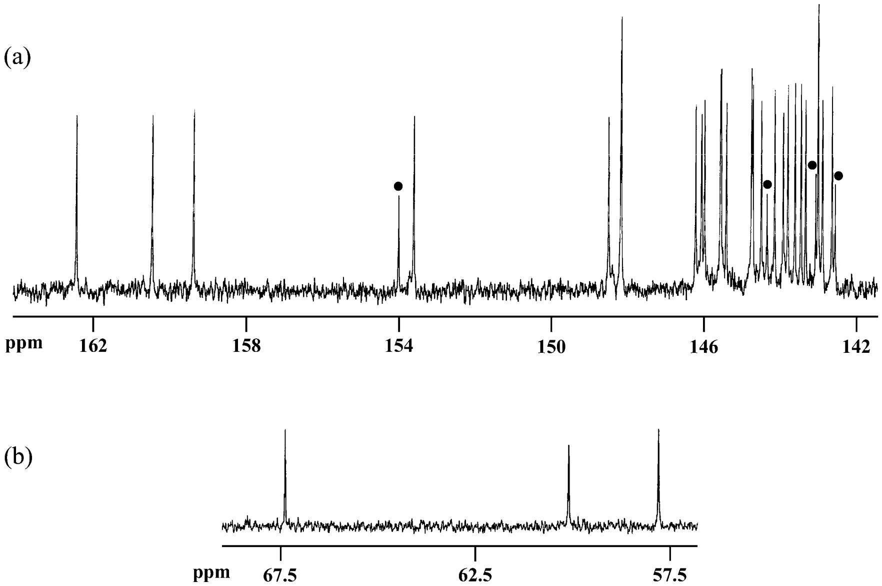


Figure 5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K, C_{60} region) of **5**.

181.3), **4b** (δ 185.4, 183.5, and 183.1), and **5** (δ 186.2). A similar trend was also reported for analogous phosphine-substituted complexes.[4b] In phosphine-substituted C_{60}-triosmium complexes, only the eq,eq-1,2-isomer and the eq,eq,eq-1,2,3-isomer have been observed in $Os_3(CO)_{9-n}(PMe_3)_n(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (n = 2 and 3) compounds,[4b] yet the tetrasubstituted compound is not known. In benzyl isocyanide-substituted C_{60}-triosmium complexes of this work, however, the eq,eq-1,2-isomer (**3a**), ax,eq-1,1-isomers (**3b**), eq,eq,eq-1,2,3-isomer (**4a**), ax,eq,eq-1,1,2-isomer (**4b**), and tetrasubstituted ax,eq,eq,eq-1,1,2,3-compound **5** have been characterized. The M−CO bond strength is known to become stronger as more electron-donating ligands are substituted on the metal center due to the increased M→CO back-donation. The carbonyl activation, therefore, is more facile with the less-electron-donating isocyanide ligand relative to the more-electron-donating phosphine ligand, which seems to facilitate the formation of higher substitution products in isocyanide-substituted complexes. Compound **5**, interestingly, exists as a single isomer with the structure found in the solid state (vide infra). For the 1,1- (**3b**) and 1,1,2-isomer (**4b**), the other possible structural isomers with eq,eq- and eq,eq,eq-configuration of the two isocyanide ligands on the Os(CO)-$(CNCH_2Ph)_2$ centers were eliminated, because the ax,eq-configuration of **3b** was clearly proved by the VT ^{13}C NMR studies of **3** (Figure S2). The two possible structural isomers of **4b** cannot be differentiated by VT ^{13}C NMR studies of **4**, since similar patterns of the VT ^{13}C NMR are expected for the two possible isomers. Moreover, the ax,eq-configuration was also observed in the structurally characterized ax,eq,eq,eq-1,1,2,3-isomer (**5**) and thus seems to be a favorable configuration for the 1,1-substituted isomer. The two isomers of **3** or **4** are apparently formed during syntheses and are not interconvertible, as indicated by NMR studies. We have not been successful as of yet in separating the two isomers of **3** or **4** and in obtaining crystal structures of **3b** and **4b**.

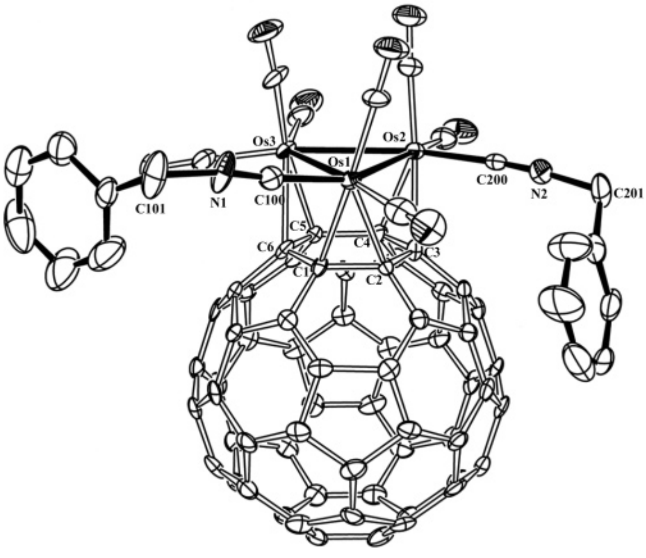


Figure 6. Molecular structure with atomic labeling scheme for **3a**.

Electrochemical Studies of 2, 3, 4, and 5. Electrochemical properties of complexes **2**−**5** have been examined by the cyclic voltammetric method in CB solutions with tetrabutylammonium perchlorate as the supporting electrolyte. Cyclic voltammograms (CVs) of **2**−**5** are shown in Figure 9. Half-wave potentials ($E_{1/2}$) of **2**−**5**, together with free C_{60}, $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**6**), $Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**7**), and $Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**8**), are provided in Table 3. All the CVs of **2**−**5** reveal four reversible redox waves that correspond to a one-electron process each with the third and fourth waves overlapped (av $\Delta E_p1 = 100$ mV, $\Delta E_p2 = 85$ mV, and $\Delta E_p3 = 103$ mV). The two isomers of **3** and **4** apparently undergo equivalent electrochemical process, respectively. The general features of the CVs of **2**−**5** are similar to those previously reported for $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**6**),[4a] as listed in Table 3. Electron delocalization from C_{60} to the triosmium cluster in **6** has been previously proposed to occur in the $\mathbf{6}^{3-}$ state based on the overlap of the third and fourth waves.[4a] As more isocyanide ligands are coordinated in **2**−**5**, all the corresponding half-wave potentials are gradually shifted to more negative potentials (ca. 80 mV), which reflects the electron-donor nature of the isocyanide ligand. The fact that the third redox couples (−1.93, −2.09, and −2.34 V) of **6**, **7**, and **8** appear at more negative potentials compared to those (−1.79, −1.84, and −1.91 V) of **2**, **3**, and **4** proves that the trimethylphosphine ligand is more electron-donating than the benzyl isocyanide ligand. Moreover, in contrast to **3**, the bis-

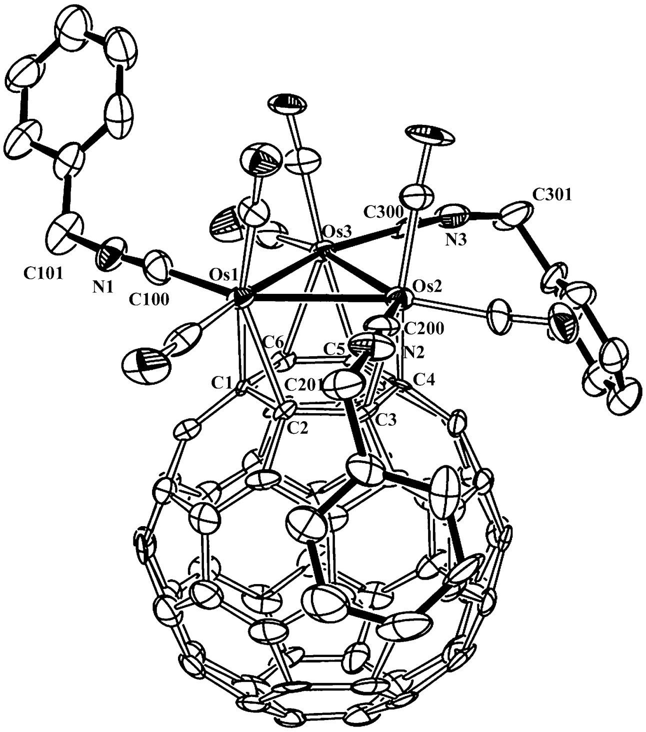


Figure 7. Molecular structure with atomic labeling scheme for **4a**.

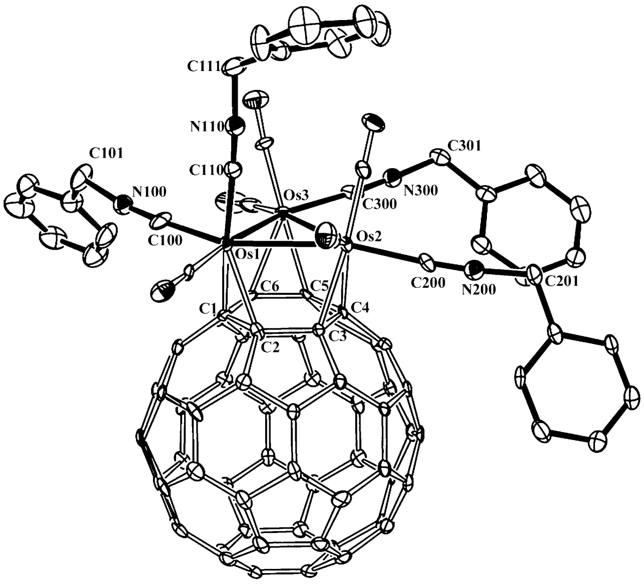


Figure 8. Molecular structure with atomic labeling scheme for **5**.

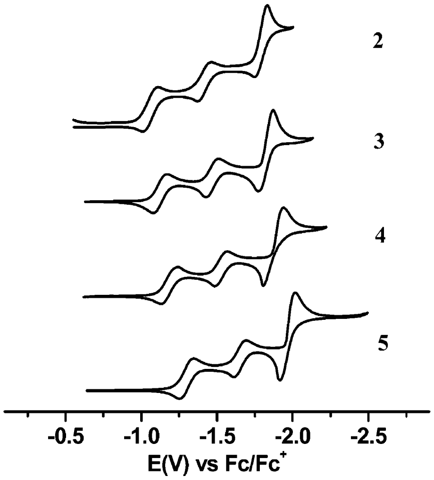


Figure 9. Cyclic voltammograms of **2**, **3**, **4**, and **5** in dry, deoxygenated chlorobenzene (0.1 M [(n-Bu)$_4$N][ClO$_4$]). Scan rate = 5 mV/s.

trimethylphosphine-substituted compound **7**[4a] exhibits three reversible one-electron redox waves without electron delocalization to the metal center due to the strong electron-donating effect of the two trimethylphosphine ligands. These are clear examples that the electrochemical properties of these C$_{60}$−metal cluster complexes can be fine-tuned by the kind and number of the attached ligands on the metal centers. The third and fourth reductions of **2**−**5** take place at the same potentials, which are even more positive (−1.79 for **2**, −1.84 for **3**, −1.91 for **4**, and −1.99 V for **5**) than the fourth reduction of free C$_{60}$ at −2.38 V. These overlaps of the third and fourth waves in **2**−**5** support the conclusion that the electron density of C$_{60}$ in **2**$^{3-}$, **3**$^{3-}$, **4**$^{3-}$, and **5**$^{3-}$ is significantly delocalized to the metal cluster center, and thus large anodic shifts of the fourth reductions relative to C$_{60}$ occur (590 mV for **2**, 540 mV for **3**, 470 mV for **4**, and 380 mV for **5**). This electron delocalization from C$_{60}$ to the metal cluster is implied by the two close redox waves and well precedented in C$_{60}$−metal cluster complexes.[3,4a,11] Although electron-donating isocyanide ligands are substituted in **2**−**5**, interestingly, the fourth electron addition to C$_{60}$ in **2**$^{3-}$, **3**$^{3-}$, **4**$^{3-}$, and **5**$^{3-}$ is still easier compared to that in free C$_{60}$$^{3-}$ due to the electron delocalization from the C$_{60}$ moiety to the triosmium center.[2a,11]

Concluding Remarks

In the present benzyl isocyanide substitution chemistry of Os$_3$(CO)$_9$(μ_3-η^2:η^2:η^2-C$_{60}$) (**1**), we observed formation of Os$_3$(CO)$_{9-n}$(CNCH$_2$Ph)$_n$(μ_3-η^2:η^2:η^2-C$_{60}$) (n = 2 (**3**), 3 (**4**), and 4 (**5**)) up to tetrasubstitution, in contrast to the phosphine substitution chemistry, due to the less-electron-donating effect of the isocyanide ligand relative to the phosphine ligand. In bis- and tris-substituted benzyl isocyanide complexes, two isomers (**3a**/**3b** and **4a**/**4b**) have been observed in solution, whereas only a single isomer has been reported to exist in analogous phosphine-substituted complexes. All the substitution reactions proceed under mild conditions with the solid (triphenylphosphino)benzylimine reagent, which is very convenient to handle and generally results in high yields, especially without the unpleasant smell of the isocyanide reagent. The slim-shaped isocyanide ligand is known to adopt an axial position on the triosmium framework,[12] which accounts for the existence of two isomers of **3** and **4** and the diversity of the benzyl isocyanide substitution chemistry. In particular, electrochemical properties of the isocyanide derivatives are quite different from those of the phosphine derivatives, which implies that investigation of the substitution chemistry is very important to prepare C$_{60}$−metal cluster complexes with various electronic properties for future applications in electronic nanomaterials and device fabrication.

Experimental Section

General Comments. All the reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques.

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[11] Park, J. T.; Cho, J.-J.; Song, H.; Jun, C.-S.; Son, Y.; Kwak, J. *Inorg. Chem.* **1997**, *36*, 2698−2699.

[12] (a) Mays, M. J.; Gavens, P. D. *J. Chem. Soc., Dalton Trans.* **1980**, 911−917. (b) Lu, K.-L.; Chen, C.-C.; Lin, Y.-W.; Hong, F.-E.; Gau, H.-M.; Gan, L.-L.; Luoh, H.-D. *J. Organomet. Chem.* **1993**, *453*, 263−267.

Table 3. Half-Wave Potentials ($E_{1/2}$ vs $E°_{Fc/Fc^+}$) of Free C_{60}, 2, 3, 4, 5, 6, 7, and 8

<table>
<tr><th>compound</th><th>$E_{1/2}^{0/-1}$</th><th>$E_{1/2}^{-1/-2}$</th><th>$E_{1/2}^{-2/-3}$</th><th>$E_{1/2}^{-3/-4}$</th><th>solvent</th><th>ref</th></tr>
<tr><td>C_{60}</td><td>−1.06</td><td>−1.43</td><td>−1.91</td><td>−2.38</td><td>CB</td><td>3</td></tr>
<tr><td>$Os_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**)</td><td>−1.06</td><td>−1.42</td><td colspan="2">−1.79</td><td>CB</td><td>this work</td></tr>
<tr><td>$Os_3(CO)_7(CNCH_2Ph)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**3**)</td><td>−1.12</td><td>−1.46</td><td colspan="2">−1.84</td><td>CB</td><td>this work</td></tr>
<tr><td>$Os_3(CO)_6(CNCH_2Ph)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**4**)</td><td>−1.19</td><td>−1.54</td><td colspan="2">−1.91</td><td>CB</td><td>this work</td></tr>
<tr><td>$Os_3(CO)_5(CNCH_2Ph)_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**5**)</td><td>−1.30</td><td>−1.65</td><td colspan="2">−1.99</td><td>CB</td><td>this work</td></tr>
<tr><td>C_{60}</td><td>−1.08</td><td>−1.46</td><td>−1.90</td><td>−2.38</td><td>DCB</td><td>4a</td></tr>
<tr><td>$Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**6**)</td><td>−1.06</td><td>−1.42</td><td>−1.93</td><td>−1.95</td><td>DCB</td><td>4a</td></tr>
<tr><td>$Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**7**)</td><td>−1.13</td><td>−1.48</td><td>−2.09</td><td></td><td>DCB</td><td>4a</td></tr>
<tr><td>$Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**8**)</td><td>−1.28</td><td>−1.66</td><td>−2.34</td><td></td><td>CB</td><td>this work</td></tr>
</table>

Solvents were dried over the appropriate drying agents and distilled immediately before use. C_{60} (99.5%, SES research) was used without further purification. $PhCH_2N{=}PPh_3$,[13] $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$,[14] and $Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$[4b] were prepared according to the literature methods. Carbon-13 CO enriched complexes were prepared by using $Os_3(^*CO)_{12}$ (ca. 50% enrichment).[15] 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) and ^{13}C (100 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 Institute, 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 $Os_3(CO)_7(CNR)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (3). Method A. A chlorobenzene solution (50 mL) of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) (50.0 mg, 0.0324 mmol) and $PhCH_2N{=}PPh_3$ (3 equiv, 35.7 mg, 0.0971 mmol) was stirred for 12 h at room temperature. Evaporation of the solvent and purification by preparative TLC (CS_2) afforded a mixture of two isomeric compounds, **3a** and **3b** (39.0 mg, 0.0227 mmol, 70%, $R_f = 0.4$), as a brown solid: IR (CH_2Cl_2) $\nu(CO)$ 2047 (vs), 2015 (s), 2002 (m), 1982 (w); $\nu(NC)$ 2183 (m) cm^{-1}; MS (FAB^+) m/z 1722 (M^+). Anal. Calcd for $C_{83}H_{14}N_2O_7Os_3$: C, 57.90; H, 0.82; N, 1.63. Found: C, 56.53; H, 0.92; N, 1.78. Compound **3a**: ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.33−7.24 (m, 10H, *Ph*), 5.08 (an overlapped AB pattern, 4H, $J_{HH} = 16.4$ Hz, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K,) carbonyl carbon; δ 182.2 (2CO), 181.6 (2CO), 179.1 (3CO), C_{60} sp^2 carbon; δ 158.2 (2C), 157.6 (2C), 155.8 (2C), 152.5 (2C), 152.3 (1C), 148.1 (2C), 148.1 (2C), 147.9 (2C), 146.3 (2C), 146.2 (2C), 146.1 (2C), 145.2 (2C), 145.1 (2C), 145.0 (2C), 144.6 (2C), 144.4 (2C), 144.3 (2C), 144.2 (2C), 144.1 (2C), 144.0 (2C), 143.8 (2C), 143.7 (1C), 143.1 (2C), 143.0 (2C+1C), 142.8 (1C), 142.5 (2C), 142.4 (2C), C_{60} sp^3 carbon; 64.1 (2C), 62.3 (2C), 54.9 (2C), benzyl isocyanide carbon; 132.2 (2C, NC), 129.2−127.0 (12C, *Ph*), 48.9 (2C, CH_2). Compound **3b**: ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.33−7.24 (m, 10H, *Ph*), 5.21 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ 181.3 (1CO), 179.3 (6CO). Other carbon signals too weak to be observed. **3a**:**3b** = 7:1 by integration of NMR signals.

Method B. A chlorobenzene solution (50 mL) of **2** (50.0 mg, 0.0306 mmol) and $PhCH_2N{=}PPh_3$ (1.5 equiv, 16.9 mg, 0.0459 mmol) was stirred for 12 h at room temperature. Evaporation of the solvent and purification by preparative TLC (CS_2) gave a mixture of two isomeric compounds, **3a** and **3b** (36.9 mg, 0.0214 mmol, 70%, $R_f = 0.4$), as a brown solid.

Preparation of $Os_3(CO)_6(CNR)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (4). Method A. A chlorobenzene solution (50 mL) of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) (50.0 mg, 0.0324 mmol) and $PhCH_2N{=}PPh_3$ (5 equiv, 59.5 mg, 0.1620 mmol) was heated at 120 °C for 3 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) afforded a mixture of two isomeric compounds, **4a** and **4b** (41.1 mg, 0.0227 mmol, 70%, $R_f = 0.6$), as a brownish-green solid: IR (CH_2Cl_2) $\nu(CO)$ 2022 (vs), 1993 (s), 1960 (m), 1936 (w); $\nu(NC)$ 2175 (s) cm^{-1}; MS (FAB^+) m/z 1811 (M^+). Anal. Calcd for $C_{90}H_{21}N_3O_6Os_3$: C, 59.69; H, 1.17; N, 2.32. Found: C, 58.21; H, 1.57; N, 2.37. Compound **4a**: ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.33−7.22 (m, 15H, *Ph*), 5.01 (s, 6H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) carbonyl carbon; δ 183.7 (6CO), C_{60} sp^2 carbon; 159.1 (6C), 153.2 (3C), 148.2 (6C), 146.1 (6C), 145.4 (6C), 144.5 (6C), 144.0 (3C), 143.9 (6C), 143.1(6C), 143.0 (3C), 142.6 (3C), C_{60} sp^3 carbon; 61.0 (6C), benzyl isocyanide carbon; 132.6 (3C, NC), 129.1−126.9 (18C, *Ph*), 48.6 (3C, CH_2). Compound **4b**: ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.33−7.22 (m, 15H, *Ph*), 5.21 (s, 2H, CH_2), 5.13 (s, 2H, CH_2), 5.04 (d, 1H, $J_{HH} = 16.4$ Hz, CH_2), 4.98 (d, 1H, $J_{HH} = 16.4$ Hz, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K), carbonyl carbon; δ 185.4 (1CO), 183.5 (1CO), 183.1 (1CO), 180.9 (3CO), C_{60} sp^2 carbon; 161.1−142.0 (54C), C_{60} sp^3 carbon; 69.7 (1C), 66.3 (1C), 60.6 (1C), 59.6 (1C), 55.8 (1C), 51.5 (1C), benzyl isocyanide carbon; 133.0 (1C, NC), 133.0 (1C, NC), 132.5 (1C, NC), 129.1−126.9 (18C, *Ph*), 48.9 (1C, CH_2), 48.7 (1C, CH_2), 48.6 (1C, CH_2). **4a**:**4b** = 1:1 by integration of NMR signals.

Method B. A chlorobenzene solution (50 mL) of **3** (50.0 mg, 0.0290 mmol) and $PhCH_2N{=}PPh_3$ (1.2 equiv, 14.3 mg, 0.0389 mmol) was heated at 120 °C for 3 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) produced a mixture of two isomeric compounds, **4a** and **4b** (36.8 mg, 0.0203 mmol, 70%, $R_f = 0.6$), as a brownish-green solid.

Preparation of $Os_3(CO)_5(CNR)_4(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (5). Method A. A chlorobenzene solution (50 mL) of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) (50.0 mg, 0.0324 mmol) and $PhCH_2N{=}PPh_3$ (10 equiv, 119.0 mg, 0.3240 mmol) was heated at reflux for 3 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) afforded compound **5** (24.6 mg, 0.0130 mmol, 40%, $R_f = 0.4$) as a green solid. Compound **4** (14.7 mg, 0.0081 mmol, 25%) was also produced by this method. Compound **5**: IR (CH_2Cl_2) ν (CO) 2000 (s), 1976 (s), 1948 (w), 1915 (w); $\nu(NC)$ 2165 (vs) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.28−7.23 (m, 20H, *Ph*), 5.12 (s, 4H, CH_2), 4.94 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) carbonyl carbon; δ 186.2 (1CO), 185.4 (2CO), 184.5 (2CO), C_{60} sp^2 carbon; 162.5 (2C), 160.5 (2C), 159.4 (2C), 154.0 (1C), 153.7 (2C), 148.5 (2C), 148.2 (4C), 146.2 (2C), 146.1 (2C), 146.0 (2C), 145.6 (2C), 145.5 (2C), 145.4 (2C), 144.7 (2C), 144.6 (2C), 144.5 (2C), 144.4 (1C), 144.1 (2C), 144.0 (2C), 143.8 (2C), 143.7 (2C), 143.5 (2C), 143.3 (2C), 143.1 (1C), 143.0 (2C), 142.9 (2C), 142.7 (2C), 142.6 (1C), C_{60} sp^3 carbon; 67.4 (2C), 60.2 (2C), 57.9 (2C), benzyl isocyanide carbon; 133.5 (2C, NC), 133.0 (2C, NC), 129.0∼126.9 (24C, *Ph*), 48.7 (2C, CH_2), 48.5 (2C, CH_2); MS (FAB^+) m/z 1900 (M^+). Anal. Calcd for $C_{97}H_{28}N_4O_5Os_3$: C, 61.32; H, 1.49; N, 2.95. Found: C, 61.41; H, 1.63; N, 3.08.

Method B. A chlorobenzene solution (50 mL) of **4** (50.0 mg, 0.0276 mmol) and $PhCH_2N{=}PPh_3$ (5 equiv, 50.7 mg, 0.138 mmol) was heated at reflux for 3 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) gave compound **5** (14.7 mg, 0.0077 mmol, 28%, $R_f = 0.4$) as a green solid.

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Table 4. Crystallographic Data for 3a, 4a, and 5

	3a	**4a**	**5**
formula	$C_{83}H_{14}N_2O_7Os_3$	$C_{90}H_{21}N_3O_6Os_3$	$C_{97}H_{28}N_4O_5Os_3$
fw	1721.56	1810.71	1899.84
system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	10.007	12.794(3)	9.9255(7)
b, Å	13.1496(2)	32.934(7)	14.3279(9)
c, Å	21.9466(3)	13.326(3)	22.9116(15)
α, deg	84.321(1)	90	73.164(2)
β, deg	89.819(1)	93.81(3)	83.004(2)
γ, deg	71.355(1)	90	75.240(2)
V, Å^3	2721.62(6)	5603(2)	3011.7(3)
Z	2	4	2
D_{calcd}, Mg m^{-3}	2.101	2.147	2.095
temp, K	273(2)	273(2)	130(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
μ, mm^{-1}	7.057	6.861	6.387
$\theta_{\mathrm{min,max}}$	1.64, 26.48	1.65, 23.00	0.93, 26.37
R_f[a]	0.0710	0.0587	0.0624
R_w[b]	0.2083	0.1157	0.1524
GOF	1.037	1.025	1.028

[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 on a AUTOLAB (PGSTAT 10, Eco Chemie, Netherlands) 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, 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 the 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. The relative number of electrons involved in each reduction process was obtained from the graph of current versus (time)$^{-1/2}$ according to the Cottrell equation.[16]

X-ray Crystallographic Studies. Crystals of **3a**, **4a**, and **5** suitable for X-ray analysis were grown by slow solvent diffusion; for **3a** with hexane into CS_2, for **4a** with methanol into CS_2/CH_2Cl_2 (3:1), and for **5** with hexane into CS_2. Diffraction data of **3a** (273 K), **4a** (273 K), and **5** (130 K) were collected on a Bruker SMART diffractometer/CCD area detector. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. The hemispheres of reflection data were collected at scan intervals of 0.5° ω with an exposure time of 20 s per frame. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Absorption corrections were performed using SADABS.[17]

Each structure was solved by direct[18] and difference Fourier methods and was refined by full-matrix least-squares methods based on F^2 (SHELX 97).[19] All non-hydrogen atoms were refined with anisotropic thermal coefficients. Details of relevant crystallographic data for **3a**, **4a**, and **5** are summarized in Table 4.

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Supporting Information Available: IR spectra of **3**−**5**, VT ^{13}C NMR spectra of **3**, and details of the crystallographic studies of **3a**, **4a**, and **5** (PDF) as well as X-ray crystallographic files for **3a**, **4a**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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