[60]Fullerene as a Versatile Four-Electron Donor Ligand

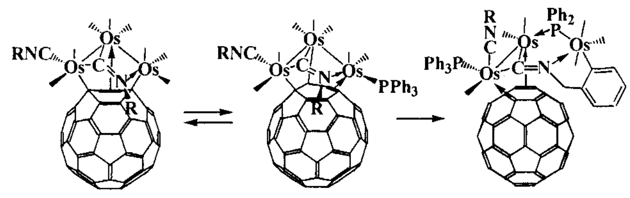
Hyunjoon Song,† Kwangyeol Lee,† Moon-Gun Choi,‡ and Joon T. Park*,†

Department of Chemistry and School of Molecular Science (BK 21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, and Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Received January 17, 2002

*Summary: A new 1,2-σ-type C_{60} compound, $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(PPh_3)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60})$ (**2**; R = CH_2Ph), is formed from $Os_3(CO)_8(CNR)(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**) upon substitution of CO with PPh_3 on a triosmium cluster framework. Compounds **1** and **2** are reversibly interconvertible. Further reaction of **2** with PPh_3 results in a π-type C_{60} complex, $Os_3(CO)_6(CNR)(\mu_3\text{-}CNCH_2C_6H_4)(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})$ (**3**), with an Os−Os bond cleavage.*

Scheme 1



$\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60}$ **1** (R = CH_2Ph) $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60}$ **2** $\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60}$ **3**

Fullerenes have attracted much current attention due to their potential applications as optical and electronic materials, superconductors, and sensors.[1] Metal cluster bound C_{60} π-complexes have shown an interesting electronic communication between C_{60} and metal centers and novel chemical reactivities.[2−5] Modification of the coordination sphere of the metal centers in C_{60}−metal cluster complexes has resulted in new C_{60} bonding modes along with interconversion among them.[5] In particular, the π-type $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ transforms to a σ-type $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60}$ on a triosmium cluster framework upon insertion of a benzyl isocyanide ligand into an Os−Os bond.[6] This provides a new synthetic route to C_{60}−metal σ-complexes, which have been rather unexplored, although such complexes are potentially useful in the selective functionalization of C_{60}.[7] Our results have opened up opportunities for further manipulation of the C_{60} bonding modes on cluster frameworks and prompted us to explore the reactivity of $Os_3(CO)_8(CNR)(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**; R = CH_2Ph)[6] toward donor phosphine ligands. Herein we wish to report the first example of a σ-type $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60}$ (1,2-σ adduct) and its reversible interconversion with $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60}$ (1,4-σ adduct) together with its conversion to a π-type $\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60}$, as shown in Scheme 1.

Decarbonylation of **1** with Me_3NO/MeCN and subsequent reaction with PPh_3 in chlorobenzene (CB) at 70 °C afforded $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(PPh_3)C_{60}$ (**2**) in 70% yield.[8] Compound **2** was quantitatively converted to **1** in CB at 100 °C under 2 atm of carbon monoxide.[9] When **2** was heated at reflux in CB for 20 min in the presence of 3 equiv of PPh_3, $Os_3(CO)_6(CNR)(\mu_3\text{-}CNCH_2C_6H_4)(PPh_3)(\mu\text{-}PPh_2)C_{60}$ (**3**) was obtained in 38% yield.[10] Compounds **2** and **3** were formulated by the molecular ion multiplet (*m/z* (highest peak) 1984 (**2**), 2140 (**3**)) in positive FAB mass spectra and by microanalytical data.

The molecular structure of **2** is shown in Figure 1.[11] The Os_3 metal framework has a linear geometry with a bent angle (∠Os(1)−Os(2)−Os(3)) of 104.7°. One benzyl isocyanide ligand is bridging all three osmium atoms

* To whom correspondence should be addressed. E-mail: jtpark@mail.kaist.ac.kr.
† Korea Advanced Institute of Science and Technology.
‡ Yonsei University.

(1) (a) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, CA, 1996. (b) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100. (c) Schön, J. H.; Kloc, Ch.; Batlogg, B. *Nature* **2000**, *408*, 549. (d) Saab, A. P.; Laub, M.; Srdanov, V. I.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 462.
(2) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123.
(3) Park, J. T.; Cho, J.-J.; Song, H. *J. Chem. Soc., Chem. Commun.* **1995**, 15.
(4) (a) Hsu, H.-F.; Shapley, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 9192. (b) Lee, K.; Hsu, H.-F.; Shapley, J. R. *Organometallics* **1997**, *16*, 3876. (c) Park, J. T.; Song, H.; Cho, J.-J.; Chung, M.-K.; Lee, J.-H.; Suh, I.-H. *Organometallics* **1998**, *17*, 227. (d) Lee, K.; Shapley, J. R. *Organometallics* **1998**, *17*, 3020. (e) Song, H.; Lee, K.; Park, J. T.; Choi, M.-G. *Organometallics* **1998**, *17*, 4477. (f) Song, H.; Lee, K.; Park, J. T.; Choi, M.-G. *J. Organomet. Chem.* **2000**, *599*, 49. (g) Song, H.; Lee, Y.; Choi, Z.-H.; Lee, K.; Park, J. T.; Kwak, J.; Choi, M.-G. *Organometallics* **2001**, *20*, 3139.
(5) Lee, K.; Lee, C. H.; Song, H.; Park, J. T.; Chang, H. Y.; Choi, M.-G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1801.
(6) Song, H.; Lee, K.; Lee, C. H.; Park, J. T.; Chang, H. Y.; Choi, M.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1500.
(7) (a) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061. (b) Zhang, S.; Brown, T. L.; Du, Y.; Shapley, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 6705. (c) Ballenweg, S.; Gleiter, R.; Krätschmer, W. *Tetrahedron Lett.* **1993**, *34*, 3737. (d) Olmstead, M. M.; Maitra, K.; Balch, A. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 231. (e) Zhu, Y.-H.; Song, L.-C.; Hu, Q.-M.; Li, C.-M. *Org. Lett.* **1999**, *1*, 1693.

(8) An acetonitrile solution (1 mL) of anhydrous Me_3NO (2.8 mg, 0.037 mmol) was added dropwise to a chlorobenzene solution (20 mL) of **1** (60.0 mg, 0.0343 mmol). The reaction mixture was stirred at room temperature for 30 min. After removal of the solvent in vacuo, the residue was dissolved in chlorobenzene (20 mL) followed by addition of PPh_3 (27.0 mg, 0.103 mmol). The resulting solution was heated at 70 °C for 4 h. Evaporation of the solvent and purification by preparative TLC (SiO_2, CS_2/CH_2Cl_2, 10:1) afforded compound **2** (47.4 mg, 0.0239 mmol, 70%, R_f = 0.5) as a black solid. IR (C_6H_{12}): ν(CO) 2059 (s), 2021 (vs), 1963 (m) cm^{-1}; ν(NC) 2182 (m), 1606 (w) cm^{-1}. ^1H NMR (400 MHz, $CS_2/CDCl_3$, 298 K): δ 7.50−6.95 (m, 25H, Ph), 5.43 (d, 1H, J_{HH} = 16 Hz, CH_2), 5.41 (d, 1H, J_{HH} = 14 Hz, CH_2), 5.36 (d, 1H, J_{HH} = 16 Hz, CH_2), 5.31 (d, 1H, J_{HH} = 14 Hz, CH_2). $^{13}C\{^1H\}$ NMR (carbonyl region, 100 MHz, $CS_2/CDCl_3$, 298 K): δ 181.6, 181.2, 180.3, 175.9, 172.2, 169.6, 166.8. $^{31}P\{^1H\}$ NMR (162 MHz, $CS_2/CDCl_3$, 298 K): δ −9.7 (s). MS (FAB^+): *m/z* 1988 [M^+]. Anal. Calcd for $C_{101}H_{29}N_2O_7Os_3P{\cdot}C_6H_4Cl_2$: C, 60.31; H, 1.56; N, 1.31. Found: C, 59.97; H, 1.75; N, 1.29.

(9) A chlorobenzene solution (20 mL) of **2** (10.0 mg, 0.005 04 mmol) was heated under 2 atm of CO pressure at 100 °C for 12 h. Evaporation of the solvent and subsequent purification by preparative TLC (SiO_2, CS_2/CH_2Cl_2, 10:1) gave **1** (8.0 mg, 0.0046 mmol, 91%).

10.1021/om020038f CCC: $22.00
Publication on Web 03/23/2002

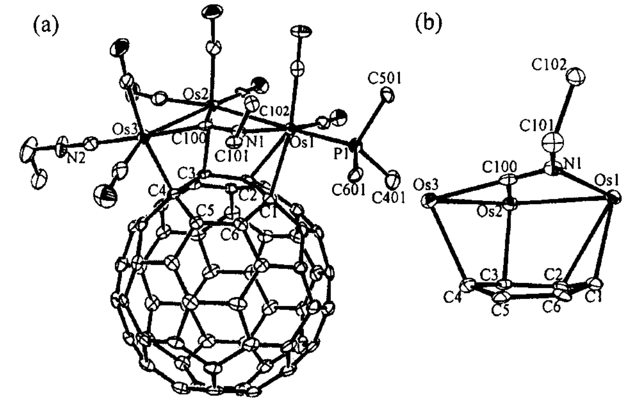


Figure 1. (a) Molecular structure of **2**. Only ipso carbon atoms of the phenyl groups are shown for clarity. (b) Expanded view of the μ_3-η^1:η^1:η^2-C_6 part of the C_{60} ligand. Selected bond lengths (Å): Os(1)−Os(2) = 2.932(1), Os(2)−Os(3) = 2.877(1), Os(1)−C(1) = 2.31(1), Os(1)−C(2) = 2.59(1), Os(2)−C(3) = 2.24(1), Os(3)−C(4) = 2.25(1), C(1)−C(2) = 1.43(1), C(2)−C(3) = 1.47(1), C(3)−C(4) = 1.57(1), C(4)−C(5) = 1.49(1), C(5)−C(6) = 1.39(1), C(6)−C(1) = 1.50(1).

in a μ_3-η^2 bonding mode, and the other is terminally coordinated on the Os(3) atom as in **1**. The PPh_3 ligand occupies an equatorial position of the Os(1) atom by replacing a carbonyl ligand. Interestingly, the carbon atoms of the C_{60} ligand bonded to the metal centers have undergone orbital rearrangement from μ_3-η^1:η^2:η^1-C_{60} in **1** (1,4-disubstituted cyclohexadiene-like) to μ_3-η^1:η^1:η^2-C_{60} (1,2-disubstituted cyclohexadiene-like) in **2** upon coordination of PPh_3. The Os(1) atom is π-coordinated by the C(1) and C(2) atoms in an η^2 mode, and the two Os(2) and Os(3) atoms are bonded to the C(3) and C(4) atoms, respectively, in a σ fashion. The σ bonds (Os(2)−C(3), 2.24(1) Å; Os(3)−C(4), 2.25(1) Å) are shorter than the π-type interactions (Os(1)−C(1), 2.31(1) Å; Os(1)−C(2), 2.59(1) Å) as previously observed in **1**.[6] The bond lengths C(1)−C(2) (1.43(1) Å) and C(5)−C(6) (1.39(1) Å) reveal a double-bond character, and the other four C−C bonds (average 1.51(1) Å) show a single-bond character, clearly indicating the 1,3-cyclohexadiene nature of the C_6 ring of C_{60}.

The structural transformation of **1** to **2** is attributed to both steric and electronic properties of PPh_3. The bulky PPh_3 ligand is coordinated at the less hindered Os(1) site among three metal centers and leads to the orbital reorganization of the C_{60} ligand. A similar reaction of **1** with PMe_3 produces $Os_3(CO)_7(CNR)(\mu_3$-$CNR)(PMe_3)(\mu_3$-η^1:η^2:η^1-$C_{60})$ (**4**), in which the smaller PMe_3 ligand merely substitutes an axial carbonyl ligand in the central Os(2) atom without changing the C_{60} bonding mode (see the Supporting Information). The metal center coordinated by the donor phosphine ligand, apparently, prefers π-interaction with C_{60} because of back-donation from the metal into C_{60}. Surprisingly, the PPh_3 is easily replaced by CO to result in clean conversion of **2** to **1**, which represents reversible interconversion between the μ_3-η^1:η^2:η^1-C_{60} and μ_3-η^1:η^1:η^2-C_{60} bonding modes.

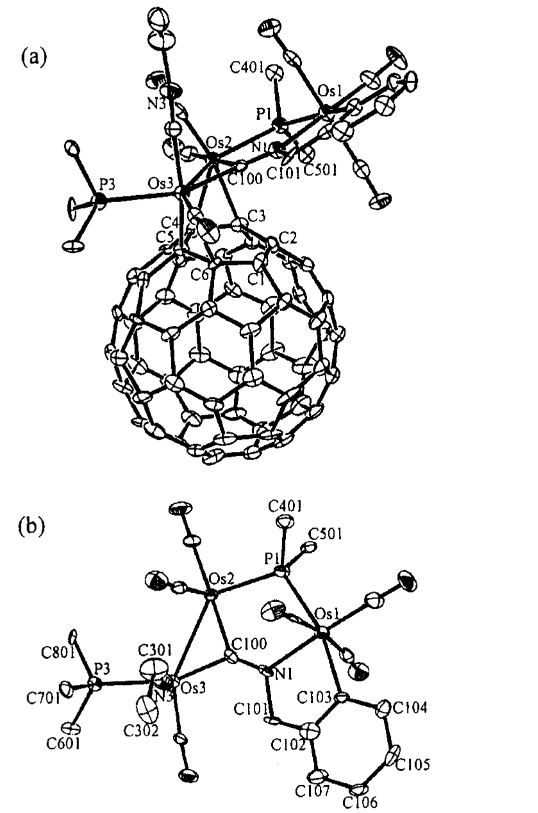


Figure 2. (a) Molecular structure of **3** and (b) a top view of the triosmium moiety in **3**. Only ipso carbon atoms of the phenyl groups are shown for clarity. Selected bond lengths (Å): Os(1)···Os(2) = 3.959(1), Os(2)−Os(3) = 2.954(1), Os(1)−N(1) = 2.12(1), Os(1)−C(103) = 2.15(1), Os(2)−C(3) = 2.22(2), Os(2)−C(4) = 2.23(2), Os(3)−C(5) = 2.25(1), Os(3)−C(6) = 2.36(1), C(1)−C(2) = 1.42(2), C(2)−C(3) = 1.49(2), C(3)−C(4) = 1.51(2), C(4)−C(5) = 1.45(2), C(5)−C(6) = 1.45(2), C(6)−C(1) = 1.43(2).

The molecular structure of **3** is shown in Figure 2.[12] The Os(1)−Os(2) bond in **2** is ruptured, and the Os(1) and Os(2) atoms are bridged by a PPh_2 ligand with a carbonyl migration from the Os(2) to the Os(1) center. The equatorial isocyanide ligand moves to an axial position, and the added PPh_3 coordinates equatorially on the Os(3) atom. The bridging isocyanide ligand is

(10) A chlorobenzene solution (10 mL) of **2** (10.0 mg, 0.00504 mmol) and PPh_3 (4.0 mg, 0.015 mmol) was heated at reflux for 20 min. Evaporation of the solvent and purification by preparative TLC (SiO_2, CS_2/CH_2Cl_2, 10:1) produced compound **3** (4.1 mg, 0.0019 mmol, 38%, R_f = 0.4) as a black solid. IR (C_6H_{12}): ν(CO) 2101 (w), 2017 (s), 1989 (vs), 1958 (m), 1918 (m) cm^{-1}; ν(NC) 2188 (m), 1568 (vw), 1542 (w) cm^{-1}. ^1H NMR (400 MHz, $CS_2/CDCl_3$, 298 K): δ 7.90−6.86 (m, 34H, Ph), 5.11 (d, 1H, J_{HH} = 19 Hz, CH_2), 4.90 (d, 1H, J_{HH} = 19 Hz, CH_2), 4.64 (d, 1H, J_{HH} = 17 Hz, CH_2), 4.18 (dd, 1H, J_{HH} = 17 Hz, J_{PH} = 2 Hz, CH_2). $^{13}C\{^1H\}$ NMR (carbonyl region, 100 MHz, $CS_2/CDCl_3$, 298 K): δ 191.4, 190.7, 184.6, 183.5, 183.0, 181.4. $^{31}P\{^1H\}$ NMR (162 MHz, $CS_2/CDCl_3$, 298 K): δ −5.5 (s), −73.4 (s). MS (FAB$^+$): *m/z* 2144 [M$^+$]. Anal. Calcd for $C_{112}H_{38}N_2O_6Os_3P_2$: C, 62.86; H, 1.79; N, 1.31. Found: C, 62.77; H, 1.91; N, 1.31.

(11) Crystal data for **2**·$C_6H_4Cl_2$: $C_{101}H_{29}N_2O_7Os_3P\cdot C_6H_4Cl_2$, triclinic, space group $P\bar{1}$, a = 12.984(3) Å, b = 13.429(2) Å, c = 22.122(4) Å, α = 107.39(3)°, β = 90.99(3)°, γ = 103.08(3)°, V = 3570(1) Å^3, Z = 2, D_{calcd} = 1.982 g cm^{-3}, μ = 5.495 mm^{-1}. A total of 21 964 reflections were collected by a Simens SMART diffractometer/CCD area detector with Mo Kα radiation (λ = 0.710 73 Å) using ω scans at 298 K. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give R = 0.0413 and R_w = 0.0960 (based on F^2) for 1039 parameters and 8700 unique reflections with $I > 2\sigma(I)$ and $1.62 < \theta < 23.00°$.

(12) Crystal data for **3**: $C_{112}H_{38}N_2O_6Os_3P_2$, triclinic, space group $P\bar{1}$, a = 13.647(3) Å, b = 17.280(4) Å, c = 19.431(4) Å, α = 98.455(4)°, β = 106.604(4)°, γ = 112.325(4)°, V = 3890(2) Å^3, Z = 2, D_{calcd} = 1.827 g cm^{-3}, μ = 4.996 mm^{-1}. A total of 23 662 reflections were collected at 233 K. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give R = 0.0648 and R_w = 0.1709 (based on F^2) for 1042 parameters and 6922 unique reflections with $I > 2\sigma(I)$ and $1.65 < \theta < 23.00°$.

bonded to all three Os centers, but the phenyl group orthometalates the Os(1) atom, forming a five-membered metallacycle ($OsNC_3$). Accompanied by a series of rearrangements, the C_{60} molecule has once again undergone orbital rearrangement to a cyclohexatriene-like C_6 ring. The Os(2) and Os(3) atoms are bonded to two adjacent double bonds (C(3)−C(4) and C(5)−C(6)) of the C_6 ring in a π-type μ-η^2:η^2-C_{60} mode.

The detailed mechanism for the conversion of **2** to **3** seems to be very complicated, but the likely pathway would involve rupture of a C_{60} π-interaction on Os(1) and subsequent orthometalation of the phenyl group of the bridging isocyanide ligand on the unsaturated Os(1) center. A benzene molecule, obviously formed by coupling of a hydride and a phenyl group from PPh_3 on the Os(1) atom, is dissociated from the molecule. The resulting PPh_2 moiety bridges the Os(1) and Os(2) atoms concomitant with a carbonyl migration from Os(2) to Os(1) and the Os(1)−Os(2) bond cleavage. Scission of the Os−Os bond induces conversion of the Os(2)−C(3) σ-bond in **2** to the Os(2)−(C(3),C(4)) π-bond in **3** for the Os(2) center to have an 18-electron configuration, which causes extensive reorganization of metal−C_{60} interactions. The PPh_3 ligand is added to the electron-deficient 16e Os(3) center formed by cleavage of the Os(3)−C(4) σ-bond in **2**. The Os(3) atom is π-coordinated to the C(5) and C(6) atoms of the C_{60} ligand by loss of a carbonyl ligand to produce **3**.

In conclusion, we have discovered a new μ_3-η^1:η^1:η^2-C_{60} bonding mode and demonstrated that three different bonding modes of the C_{60} ligand as a four-electron donor, μ_3-η^1:η^2:η^1-, μ_3-η^1:η^1:η^2-, and μ-η^2:η^2-C_{60}, are interconvertible (**1** $\leftrightarrows$ **2** $\rightarrow$ **3**) on the Os_3 cluster framework. Furthermore, we have developed a novel and very useful methodology for the transformation between σ- and π-bonds in C_{60}−metal cluster complexes by controlling the steric and electronic properties of the metal centers. Efforts are currently underway with **1** and **2** to selectively functionalize the C_{60} molecule and prepare various 1,4- and 1,2-adducts of C_{60}.

Acknowledgment. This work was supported by the National Research Laboratory (NRL) Program of the Korean Ministry of Science & Technology (MOST) and the Korea Science Engineering Foundation (Project No. 1999-1-122-001-5).

Supporting Information Available: Text giving details on the synthesis of **4** and text, tables and figures giving details of the X-ray crystallographic and structural data for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020038F