

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

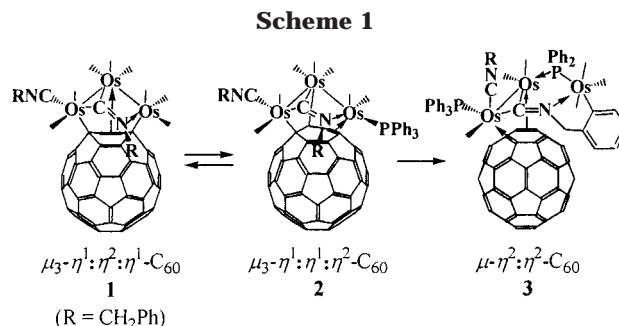
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**Summary:** A new 1,2- $\sigma$ -type  $C_{60}$  compound,  $Os_3(CO)_7(CNR)(\mu_3-CNR)(PPh_3)(\mu_3-\eta^1:\eta^1:\eta^2-C_{60})$  (**2**;  $R = CH_2Ph$ ), is formed from  $Os_3(CO)_8(CNR)(\mu_3-CNR)(\mu_3-\eta^1:\eta^2:\eta^1-C_{60})$  (**1**) upon 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  $\pi$ -type  $C_{60}$  complex,  $Os_3(CO)_6(CNR)(\mu_3-CNCH_2C_6H_4)-(PPh_3)(\mu-PPh_2)(\mu-\eta^2:\eta^2-C_{60})$  (**3**), with an Os–Os bond cleavage.

Fullerenes have attracted much current attention due to their potential applications as optical and electronic materials, superconductors, and sensors.<sup>1</sup> Metal cluster bound  $C_{60}$   $\pi$ -complexes have shown an interesting electronic communication between  $C_{60}$  and metal centers and novel chemical reactivities.<sup>2–5</sup> 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.<sup>5</sup> In particular, the  $\pi$ -type  $\mu_3-\eta^2:\eta^2:\eta^2-C_{60}$  transforms to a  $\sigma$ -type  $\mu_3-\eta^1:\eta^2:\eta^1-C_{60}$  on a triosmium cluster framework upon insertion of a benzyl isocyanide ligand into an Os–Os bond.<sup>6</sup> This provides a new synthetic route to  $C_{60}$ –metal  $\sigma$ -complexes, which have been rather unexplored, although such complexes are potentially useful in the selective functionalization of  $C_{60}$ .<sup>7</sup> 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  $Os_3(CO)_8(CNR)(\mu_3-CNR)(\mu_3-\eta^1:\eta^2:\eta^1-C_{60})$  (**1**;  $R = CH_2Ph$ )<sup>6</sup> toward donor phosphine ligands. Herein we wish to report the first example of a  $\sigma$ -type  $\mu_3-\eta^1:\eta^1:\eta^2-C_{60}$  (1,2- $\sigma$  adduct) and its reversible interconversion with  $\mu_3-\eta^1:\eta^2:\eta^1-C_{60}$  (1,4- $\sigma$  adduct) together with its conversion to a  $\pi$ -type  $\mu-\eta^2:\eta^2-C_{60}$ , 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  $Os_3(CO)_7(CNR)(\mu_3-CNR)(PPh_3)C_{60}$  (**2**) in 70% yield.<sup>8</sup> Compound **2** was quantitatively converted to **1** in CB at 100 °C under 2 atm of carbon monoxide.<sup>9</sup> When **2** was heated at reflux in CB for 20 min in the presence of 3 equiv of  $PPh_3$ ,  $Os_3(CO)_6(CNR)(\mu_3-CNCH_2C_6H_4)-(PPh_3)(\mu-PPh_2)C_{60}$  (**3**) was obtained in 38% yield.<sup>10</sup> 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.<sup>11</sup> The  $Os_3$  metal framework has a linear geometry with a bent angle ( $\angle Os(1)-Os(2)-Os(3)$ ) of 104.7°. One benzyl isocyanide ligand is bridging all three osmium atoms

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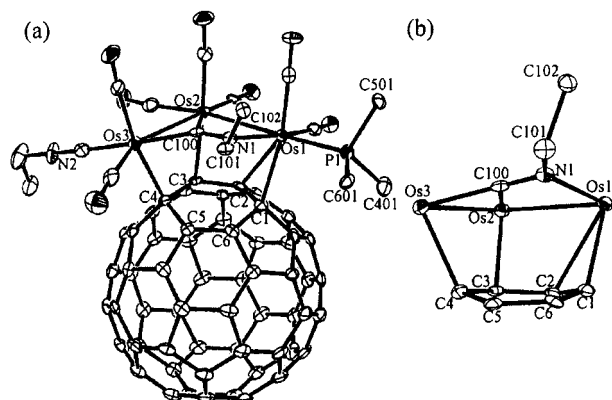
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(8) An acetonitrile solution (1 mL) of anhydrous  $Me_3NO$  (2.8 mg, 0.037 mmol) was added dropwise to a chlorobenzene solution (20 mL) of **1** (60.0 mg, 0.0343 mmol). The reaction mixture was stirred at room temperature for 30 min. After removal 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 ( $C_6H_{12}$ ):  $\nu(CO)$  2059 (s), 2021 (vs), 1963 (m)  $cm^{-1}$ ;  $\nu(NC)$  2182 (m), 1606 (w)  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CS_2/CDCl_3$ , 298 K):  $\delta$  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,  $CH_2$ ).  $^{13}C$  NMR (carbonyl region, 100 MHz,  $CS_2/CDCl_3$ , 298 K):  $\delta$  181.6, 181.2, 180.3, 175.9, 172.2, 169.6, 166.8.  $^{31}P$  NMR (162 MHz,  $CS_2/CDCl_3$ , 298 K):  $\delta$  -9.7 (s). MS (FAB<sup>+</sup>):  $m/z$  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.

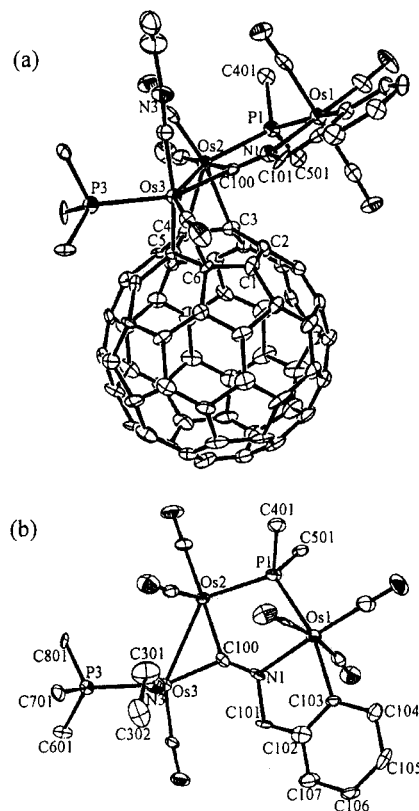
(9) A chlorobenzene solution (20 mL) of **2** (10.0 mg, 0.005 04 mmol) was heated under 2 atm of CO pressure at 100 °C for 12 h. Evaporation of the solvent and subsequent purification by preparative TLC ( $SiO_2$ ,  $CS_2/CH_2Cl_2$ , 10:1) gave **1** (8.0 mg, 0.0046 mmol, 91%).



**Figure 1.** (a) Molecular structure of **2**. Only ipso carbon atoms of the phenyl groups are shown for clarity. (b) Expanded view of the  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-C}_{60}$  part of the  $\text{C}_{60}$  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  $\mu_3\text{-}\eta^2$  bonding mode, and the other is terminally coordinated on the Os(3) atom as in **1**. The  $\text{PPh}_3$  ligand occupies an equatorial position of the Os(1) atom by replacing a carbonyl ligand. Interestingly, the carbon atoms of the  $\text{C}_{60}$  ligand bonded to the metal centers have undergone orbital rearrangement from  $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-C}_{60}$  in **1** (1,4-disubstituted cyclohexadiene-like) to  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-C}_{60}$  (1,2-disubstituted cyclohexadiene-like) in **2** upon coordination of  $\text{PPh}_3$ . The Os(1) atom is  $\pi$ -coordinated by the C(1) and C(2) atoms in an  $\eta^2$  mode, and the two Os(2) and Os(3) atoms are bonded to the C(3) and C(4) atoms, respectively, in a  $\sigma$  fashion. The  $\sigma$  bonds (Os(2)–C(3), 2.24(1) Å; Os(3)–C(4), 2.25(1) Å) are shorter than the  $\pi$ -type interactions (Os(1)–C(1), 2.31(1) Å; Os(1)–C(2), 2.59(1) Å) as previously observed in **1**.<sup>6</sup> 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  $\text{C}_6$  ring of  $\text{C}_{60}$ .

The structural transformation of **1** to **2** is attributed to both steric and electronic properties of  $\text{PPh}_3$ . The bulky  $\text{PPh}_3$  ligand is coordinated at the less hindered



**Figure 2.** (a) Molecular structure of **3** and (b) a top view of the trismium 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).

Os(1) site among three metal centers and leads to the orbital reorganization of the  $\text{C}_{60}$  ligand. A similar reaction of **1** with  $\text{PMe}_3$  produces  $\text{Os}_3(\text{CO})_7(\text{CNR})(\mu_3\text{-CNR})(\text{PMe}_3)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-C}_{60})$  (**4**), in which the smaller  $\text{PMe}_3$  ligand merely substitutes an axial carbonyl ligand in the central Os(2) atom without changing the  $\text{C}_{60}$  bonding mode (see the Supporting Information). The metal center coordinated by the donor phosphine ligand, apparently, prefers  $\pi$ -interaction with  $\text{C}_{60}$  because of back-donation from the metal into  $\text{C}_{60}$ . Surprisingly, the  $\text{PPh}_3$  is easily replaced by CO to result in clean conversion of **2** to **1**, which represents reversible interconversion between the  $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-C}_{60}$  and  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-C}_{60}$  bonding modes.

The molecular structure of **3** is shown in Figure 2.<sup>12</sup> The Os(1)–Os(2) bond in **2** is ruptured, and the Os(1) and Os(2) atoms are bridged by a  $\text{PPh}_2$  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  $\text{PPh}_3$  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  $\text{PPh}_3$  (4.0 mg, 0.015 mmol) was heated at reflux for 20 min. Evaporation of the solvent and purification by preparative TLC ( $\text{SiO}_2$ ,  $\text{CS}_2/\text{CH}_2\text{Cl}_2$ , 10:1) produced compound **3** (4.1 mg, 0.0019 mmol, 38%,  $R_f$  = 0.4) as a black solid. IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$  2101 (w), 2017 (s), 1989 (vs), 1958 (m), 1918 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{NC})$  2188 (m), 1568 (vw), 1542 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2/\text{CDCl}_3$ , 298 K):  $\delta$  7.90–6.86 (m, 34H, Ph), 5.11 (d, 1H,  $J_{\text{HH}} = 19$  Hz,  $\text{CH}_2$ ), 4.90 (d, 1H,  $J_{\text{HH}} = 19$  Hz,  $\text{CH}_2$ ), 4.64 (d, 1H,  $J_{\text{HH}} = 17$  Hz,  $\text{CH}_2$ ), 4.18 (dd, 1H,  $J_{\text{HH}} = 17$  Hz,  $J_{\text{PH}} = 2$  Hz,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (carbonyl region, 100 MHz,  $\text{CS}_2/\text{CDCl}_3$ , 298 K):  $\delta$  191.4, 190.7, 184.6, 183.5, 183.0, 181.4.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CS}_2/\text{CDCl}_3$ , 298 K):  $\delta$  –5.5 (s), –73.4 (s). MS (FAB<sup>+</sup>):  $m/z$  2144 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{112}\text{H}_{38}\text{N}_2\text{O}_6\text{Os}_3\text{P}_2$ : C, 62.86; H, 1.79; N, 1.31. Found: C, 62.77; H, 1.91; N, 1.31.

(11) Crystal data for  $\text{2-C}_6\text{H}_4\text{Cl}_2$ :  $\text{C}_{101}\text{H}_{29}\text{N}_2\text{O}_7\text{Os}_3\text{P-C}_6\text{H}_4\text{Cl}_2$ , triclinic, space group  $P\bar{1}$ ,  $a = 12.984(3)$  Å,  $b = 13.429(2)$  Å,  $c = 22.122(4)$  Å,  $\alpha = 107.39(3)^\circ$ ,  $\beta = 90.99(3)^\circ$ ,  $\gamma = 103.08(3)^\circ$ ,  $V = 3570(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.982$  g  $\text{cm}^{-3}$ ,  $\mu = 5.495$  mm<sup>–1</sup>. A total of 21 964 reflections were collected by a Siemens SMART diffractometer/CCD area detector with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\omega$  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  $1.62 < \theta < 23.00^\circ$ .

(12) Crystal data for **3**:  $\text{C}_{112}\text{H}_{38}\text{N}_2\text{O}_6\text{Os}_3\text{P}_2$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.647(3)$  Å,  $b = 17.280(4)$  Å,  $c = 19.431(4)$  Å,  $\alpha = 98.455(4)^\circ$ ,  $\beta = 106.604(4)^\circ$ ,  $\gamma = 112.325(4)^\circ$ ,  $V = 3890(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.827$  g  $\text{cm}^{-3}$ ,  $\mu = 4.996$  mm<sup>–1</sup>. 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  $1.65 < \theta < 23.00^\circ$ .

bonded to all three Os centers, but the phenyl group orthometalates the Os(1) atom, forming a five-membered metallacycle (OsNC<sub>3</sub>). Accompanied by a series of rearrangements, the C<sub>60</sub> molecule has once again undergone orbital rearrangement to a cyclohexatriene-like C<sub>6</sub> 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<sub>6</sub> ring in a  $\pi$ -type  $\mu$ - $\eta^2$ : $\eta^2$ -C<sub>60</sub> 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<sub>60</sub>  $\pi$ -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<sub>3</sub> on the Os(1) atom, is dissociated from the molecule. The resulting PPh<sub>2</sub> 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)  $\sigma$ -bond in **2** to the Os(2)–(C(3),C(4))  $\pi$ -bond in **3** for the Os(2) center to have an 18-electron configuration, which causes extensive reorganization of metal–C<sub>60</sub> interactions. The PPh<sub>3</sub> ligand is added to the electron-deficient 16e Os(3) center formed by cleavage of the Os(3)–C(4)  $\sigma$ -bond in **2**. The Os(3) atom is  $\pi$ -coordinated to the C(5) and C(6) atoms of the C<sub>60</sub> ligand by loss of a carbonyl ligand to produce **3**.

In conclusion, we have discovered a new  $\mu_3$ - $\eta^1$ : $\eta^1$ : $\eta^2$ -C<sub>60</sub> bonding mode and demonstrated that three different bonding modes of the C<sub>60</sub> ligand as a four-electron donor,  $\mu_3$ - $\eta^1$ : $\eta^2$ : $\eta^1$ -,  $\mu_3$ - $\eta^1$ : $\eta^1$ : $\eta^2$ -, and  $\mu$ - $\eta^2$ : $\eta^2$ -C<sub>60</sub>, are interconvertible (**1**  $\rightleftharpoons$  **2**  $\rightarrow$  **3**) on the Os<sub>3</sub> cluster framework. Furthermore, we have developed a novel and very useful methodology for the transformation between  $\sigma$ - and  $\pi$ -bonds in C<sub>60</sub>–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<sub>60</sub> molecule and prepare various 1,4- and 1,2-adducts of C<sub>60</sub>.

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**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>.

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