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

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Various η^2-C_{60} and μ_3-η^2,η^2,η^2-C_{60} triosmium carbonyl cluster complexes $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$ (**1**), $Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})$ (**2**), $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ (**3**), $Os_3(CO)_9(PR_3)_2(\eta^2\text{-}C_{60})$ (**4**, R = Ph; **5**, R = Me), $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**6**), and $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**7**) have been isolated as crystalline solids and characterized by spectroscopic (IR, MS, and ^1H, ^{31}P, and ^{13}C NMR) and analytical data. The molecular structure of complex **1** has been determined by a single-crystal X-ray diffraction study. The structure of **1** is derived from that of $Os_3(CO)_{12}$ by replacing an equatorial carbonyl ligand with an η^2-C_{60} ligand coordinated through a 6−6 ring fusion. The structural assignment of **2**−**7** is made on the basis of spectroscopic results. Compound **2** exists as two isomers in solution in a ratio of 2:1 (**2a**:**2b**). VT ^{13}C NMR spectra of **2a** and **5** indicate that both complexes undergo similar fluxional processes of restricted equilibration of in-plane equatorial C_{60} and carbonyl ligands via a triply bridged intermediate with identical values of $\Delta G_c^{\ddagger} = 12.7 \pm 0.1$ kcal/mol. Thermolysis of **2** in refluxing chlorobenzene affords $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**6**) in 23% yield, which can be alternatively prepared in 32% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ (2 equiv) and C_{60} (1 equiv). Decarbonylation of **6** with Me_3NO/MeCN reagent in the presence of excess PMe_3 gives $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**7**) in a quantitative yield. VT ^{13}C NMR spectra of both **6** and **7** reveal a localized-3-fold rotation of carbonyl and phosphine ligands on each osmium center.

Introduction

The organometallic chemistry of C_{60} has attracted much attention[1] concerning the effect of metal coordination on the properties of C_{60} since the discovery[2] and macroscopic synthesis[3] of C_{60}. The first structurally characterized complex, $(C_{60})(OsO_4)(4\text{-}^tBuC_5H_4N)_2$, an osmate ester with C−O−Os bonds, was reported by Hawkins and co-workers.[4] However, the first example with a direct metal−C_{60} bond, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, was reported by Fagan *et al.*[5] Numerous reports of other metal-coordinated C_{60} complexes have included those of Ta, Mo, W, Fe, Ru, Co, Rh, Ir, Ni, and Pd, in which all the mononuclear metals are bound in an η^2-fashion at the 6−6 ring fusion.[6] The C_{60} ligand in these complexes acts as an electronegative alkene.[1a,6j] Subsequent development in metal−C_{60} π-complex chemistry has led to the synthesis of μ-η^2,η^2-C_{60} complexes, $(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})[Ir_2Cl_2(1,5\text{-COD})_2]_2$[7] and $(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})Cp'_2Ru_2(\mu\text{-}Cl)_2$ ($Cp' = \eta^5\text{-}C_5Me_5$),[8] in which the metal atoms occupy the adjacent π-bonds of a six-membered ring of C_{60} like diene complexes. We set out to investigate complexes of C_{60} with transition metal clusters with the expectation of seeing new bonding modes, physical properties, fluxionality, or reactivities of C_{60} in these complexes by cooperative interactions of the metal centers. We have prepared various C_{60}−triosmium carbonyl cluster complexes, $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$ (**1**), $Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})$ (**2**), $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ (**3**), $Os_3(CO)_9(PR_3)_2(\eta^2\text{-}C_{60})$ (**4**, R = Ph; **5**, R = Me), $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**6**), and

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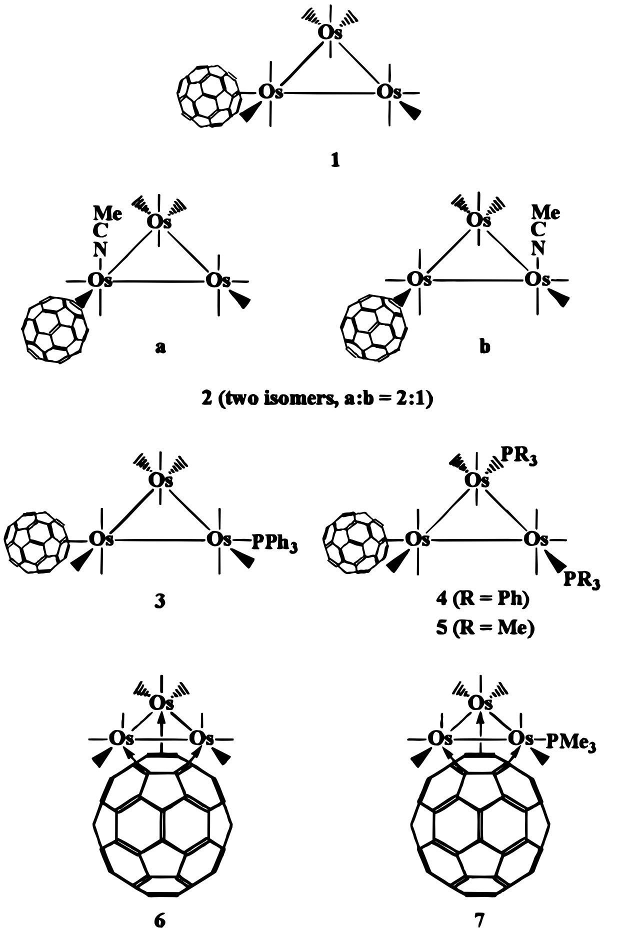
Chart 1. Structures of 1−7



$Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**7**), both η^2-C_{60} (**1**−**5**) and $\mu_3\text{-}\eta^2,\eta^2,\eta^2$-$C_{60}$ (**6** and **7**) triosmium complexes.

Transition metal cluster-bound C_{60} complexes were unknown prior to this work. The first arene-like complex of C_{60}, $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[9] however, has been recently prepared from the reaction of $Ru_3(CO)_{12}$ and C_{60} in hexane under reflux for 2 days in a very low (4%) yield by Shapley and co-workers during our investigation. In preliminary forms, we have reported the synthesis and characterization of complexes **1**, **2**, **3**, and **4**.[10] Electrochemical studies of **1**, **3**, and **4** have revealed the first example of C_{60}-mediated electron transfer to the metal center.[11] Since then, we have completed the structural characterization of **1** and fluxional processes of **2** and **5**. Furthermore, reactivity studies of **2** have resulted in high-yield syntheses of $\mu_3\text{-}\eta^2,\eta^2,\eta^2$-$C_{60}$ triosmium complexes, **6** and **7**. Herein we report the preparation and characterization of triosmium cluster derivatives of C_{60}, **1**−**7**, as shown in Chart 1.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Solvents were appropriately dried before use. C_{60} (99.8%, Gold grade, Hoechst AG) was used without further purification. Anhydrous trimethylamine *N*-oxide (mp 225−230 °C) was obtained from $Me_3NO{\cdot}2H_2O$ (98%, Aldrich Chemical Ltd.) by sublimation (3 times) at 90−100 °C under vacuum. $Os_3(CO)_{11}(NCMe)$,[12] $Os_3(CO)_{11}(PR_3)$,[12] and $Os_3(CO)_{10}(PR_3)_2$ (R = Ph, Me)[13] were prepared by literature methods. Carbon-13 (*C) CO-enriched complexes were prepared by using $Os_3(^*CO)_{12}$[14] (*ca.* 50% enrichment). Preparative thin-layer plates were prepared from silica gel GF_{254} (type 60, E. Merck).

Infrared spectra were obtained on a Bomem MB-100 FT-IR spectrometer. ^1H NMR (300 MHz), ^{13}C NMR (75 or 151 MHz), and ^{31}P NMR (122 MHz) spectra were recorded on either a Bruker AM-300 or DMX-600 spectrometer. FAB positive-ion mass spectra (FAB$^+$) were obtained by the staff of the Korea Basic Science Center. All *m/z* values are referenced to ^{192}Os. Elemental analyses were provided by the staff of the Agency for Defense Development.

Preparation of $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$ (1). A toluene solution (30 mL) of $Os_3(CO)_{11}(NCMe)$ (20.0 mg, 0.0217 mmol) and C_{60} (20.0 mg, 0.0278 mmol) was heated at 80 °C for 5 min to give a dark brown solution. The solvent was evaporated and the residue was purified by preparative TLC (toluene:hexane, 1:2) at −15 °C to afford compound **1** (18.4 mg, 0.0115 mmol, 53%, $R_f = 0.7$) as a black microcrystalline solid. IR (CH_2Cl_2) ν(CO) 2122 (m), 2074 (s), 2059 (m), 2038 (vs), 2016 (m), 2006 (m), 1990 (w) cm^{-1}; ^{13}C NMR (toluene-d_8, 298 K) δ 183.3 (2 CO), 182.9 (2 CO), 181.7 (2 CO), 172.0 (1 CO), 171.9 (1 CO), 170.3 (1 CO), 168.8 (1 CO), 168.5 (1 CO); MS (FAB$^+$) *m/z* 1604 (M$^+$). Anal. Calcd for $C_{78}H_8O_{11}Os_3$ (**1**·toluene): C, 55.39; H, 0.48. Found: C, 55.33; H, 0.35.

Preparation of $Os_3(CO)_{10}(NCMe)(\eta^2\text{-}C_{60})$ (2). A dichloromethane (20 mL)−acetonitrile (3 mL) solution of $Os_3(CO)_{11}(NCMe)$ (20.0 mg, 0.0217 mmol) was treated with an acetonitrile solution (3 mL) of anhydrous Me_3NO (1.7 mg, 0.023 mmol) at room temperature for 30 min. After evaporation of the solvent *in vacuo*, a toluene (30 mL) solution of C_{60} (20.0 mg, 0.0278 mmol) was added to the residue. The resulting solution was heated at 80 °C for 30 min to give a dark green solution. The solvent was evaporated, and the residue was purified by preparative TLC (toluene:hexane, 1:1) at −15 °C to afford a mixture of two isomeric compounds **2** (27.3 mg, 0.0169 mmol, 78%, $R_f = 0.5$) as a black solid. IR (CH_2Cl_2) ν(CO) 2110 (m), 2101 (w), 2064 (s), 2055 (m), 2032 (s), 2018 (vs), 1988 (m), 1958 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 298 K) δ 3.02 (s, 3H, CH_3CN, **2a**), 2.85 (s, 3H, CH_3CN, **2b**), [**2a**]:[**2b**] = 2:1; ^{13}C NMR (CD_2Cl_2, 193 K) δ 187−183 (4 CO), 181.6, 176.9, 174.6, 173.3, 170.0, 169.2 (CO's of major isomer **2a** from an isomeric mixture); MS (FAB$^+$) *m/z* 1617 (M$^+$). Anal. Calcd for $C_{72}H_3O_{10}NOs_3$: C, 53.63; H, 0.19. Found: C, 53.81; H, 0.18.

Interconversion of 1 and 2. 1 → 2: Compound **1** (10.0 mg, 0.0063 mmol) was dissolved in a mixture of toluene (20 mL) and acetonitrile (3 mL). The solution was cooled to −50 °C, and an acetonitrile solution (3 mL) of anhydrous Me_3NO (0.5 mg, 0.007 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature for 2 h. Evaporation of the solvent and purification by preparative TLC (toluene:hexane, 1:1) at −15 °C gave compound **2** (9.1 mg, 0.0056 mmol, 90%). **2 → 1**: Carbon monoxide was bubbled with a gas dispersion tube through a toluene solution (20 mL) of compound **2** (10.0 mg, 0.0062 mmol) at room temperature for 2 h. The solvent was evaporated, and the residue was purified by preparative TLC (toluene:hexane, 1:2) at −15 °C to give compound **1** (9.4 mg, 0.0059 mmol, 95%).

Preparation of $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ (3). A dichloromethane (20 mL)−acetonitrile (3 mL) solution of $Os_3(CO)_{11}$-

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(PPh_3) (20.0 mg, 0.0175 mmol) was treated with an acetonitrile solution (3 mL) of anhydrous Me_3NO (1.5 mg, 0.020 mmol) at room temperature for 30 min. After evaporation of the solvent *in vacuo*, a toluene solution (30 mL) of C_{60} (16.4 mg, 0.0228 mmol) was added to the residue. The solution was stirred at room temperature for 4 h to give a green solution. The solvent was evaporated, and the residue was purified by preparative TLC (toluene:hexane, 1:1) at −15 °C to afford compound **3** (26.7 mg, 0.0146 mmol, 83%, $R_f = 0.8$) as a black microcrystalline solid. IR (CH_2Cl_2) ν(CO) 2099 (m), 2051 (m), 2034 (m), 2017 (vs), 1993 (m), 1975 (sh) cm^{-1}; MS (FAB^+) *m/z* 1838 (M^+). Anal. Calcd for $C_{88}H_{15}O_{10}POs_3$: C, 57.64; H, 0.82. Found: C, 56.77; H, 0.90.

Conversion of 2 to 3. Compound **2** (10.0 mg, 0.0062 mmol) was dissolved in toluene (20 mL), and then PPh_3 (3.3 mg, 0.013 mmol) was added. The reaction mixture was stirred for 1 h at room temperature, and the solvent was evaporated. Purification by preparative TLC (toluene:hexane, 1:1) at −15 °C afforded compound **3** (10.9 mg, 0.0059 mmol, 96%).

Preparation of $Os_3(CO)_9(PR_3)_2(\eta^2\text{-}C_{60})$ (R = Ph (4), Me (5)). A dichloromethane (20 mL)−acetonitrile (3 mL) solution of $Os_3(CO)_{10}(PPh_3)_2$ (20.0 mg, 0.0145 mmol) was treated with an acetonitrile solution (3 mL) of anhydrous Me_3NO (1.2 mg, 0.016 mmol) at room temperature for 30 min. After evaporation of the solvent *in vacuo*, the residue was dissolved in toluene (30 mL) containing C_{60} (13.6 mg, 0.0189 mmol). The resulting solution was stirred at room temperature for 4 h to give a blue-green solution. The solvent was evaporated and the residue was purified by preparative TLC (toluene:hexane, 1:1) at −15 °C to produce compound **4** (19.5 mg, 0.00945 mmol, 65%, $R_f = 0.5$) as a black solid. The reaction of $Os_3(CO)_{10}(PMe_3)_2$ (20.0 mg, 0.0199 mmol) with anhydrous Me_3NO (1.6 mg, 0.022 mmol) followed by treatment with C_{60} (18.7 mg, 0.0259 mmol) was carried out following a procedure similar to that for **4**. Evaporation of the solvent and purification by preparative TLC (toluene:hexane, 2:1) at −15 °C produced compound **5** (16.6 mg, 0.00979 mmol, 49%, $R_f = 0.6$) as a black solid. Compound **4**: IR (CH_2Cl_2) ν(CO) 2109 (w), 2083 (w), 2072 (w), 2051 (m), 2017 (s), 1999 (vs), 1964 (m), 1941 (sh) cm^{-1}; MS (FAB^+) *m/z* 2072 (M^+). Anal. Calcd for $C_{105}H_{30}O_9P_2Os_3$: C, 60.99; H, 1.46. Found: C, 59.67; H, 1.46. Compound **5**: IR (CH_2Cl_2) ν(CO) 2069 (m), 2016 (sh), 2007 (s), 1990 (vs), 1966 (sh), 1954 (s) cm^{-1}; ^1H NMR (CD_2Cl_2, 298 K) δ 2.04 (d, $^2J_{PH} = 10.3$ Hz, 18H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 213 K) δ −49.29 (s), −50.87 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 213 K) δ 194.8 ($^2J_{CP} = 7.2$ Hz, 2 CO), 194.5 ($^2J_{CP} = 8.1$ Hz, 2 CO), 185.4 (2 CO), 181.6 (1 CO), 180.6 (1 CO), 178.3 (1 CO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ 161.3, 147.6, 146.9, 145.8, 145.7, 145.3, 145.2, 145.1, 144.8, 144.2, 144.1, 143.3, 142.9, 142.7, 142.3, 141.4 (16 C_{60} signals), 56.5 (C_{60} sp^3 carbon), 22.6, 22.2 (br, $P(CH_3)_3$); MS (FAB^+) *m/z* 1700 (M^+). Anal. Calcd for $C_{75}H_{18}O_9P_2Os_3$:C, 53.13; H, 1.07. Found: C, 53.41; H, 1.33.

Conversion of 3 to 4. Compound **3** (10.0 mg, 0.0055 mmol) was dissolved in toluene (20 mL), and PPh_3 (2.9 mg, 0.011 mmol) was added. The solution was cooled to −50 °C, and a solution of anhydrous Me_3NO (0.5 mg, 0.007 mmol) in acetonitrile (3 mL) was added dropwise. The mixture was allowed to warm to room temperature for 2 h. The solvent was evaporated, and the residue was purified by preparative TLC (toluene:hexane, 1:1) at −15 °C to afford compound **4** (10.3 mg, 0.0050 mmol, 91%).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (6). To a dichloromethane (30 mL) and acetonitrile (5 mL) solution of $Os_3(CO)_{11}(NCMe)$ (50.0 mg, 0.0544 mmol) was added an acetonitrile solution (3 mL) of anhydrous Me_3NO (4.5 mg, 0.060 mmol) dropwise at room temperature. After evaporation of the solvent *in vacuo*, the residue was dissolved in chlorobenzene (5 mL). The solution was added dropwise to a refluxing chlorobenzene solution of C_{60} (20.0 mg, 0.0278 mmol, 0.5 equiv), and the reaction mixture was stirred for 90 min. The solvent was evaporated, and the residue was purified by preparative TLC (CS_2) to give compound **6** (13.7 mg, 0.00888 mmol, 32%, $R_f = 0.8$) as a reddish-brown solid. IR (CS_2) ν(CO) 2081 (s), 2046 (vs), 2016 (m), 2002 (m), 1983 (sh) cm^{-1}; ^{13}C NMR (CS_2/ext. CD_2Cl_2, 298 K) δ 176.1 (s, 9 CO); MS (FAB^+) *m/z* 1548 (M^+). Anal. Calcd for $C_{69}O_9Os_3$:C, 53.70. Found: C, 53.94.

Thermolysis of 2. A chlorobenzene solution (20 mL) of compound **2** (10.0 mg, 0.0062 mmol) was heated at reflux for 1 h. After evaporation of the solvent *in vacuo*, the residue was purified by preparative TLC (CS_2) to afford compound **6** (2.2 mg, 0.0014 mmol, 23%).

Preparation of $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (7). $Os_3(CO)_{11}(PMe_3)$ (50.0 mg, 0.0524 mmol) was dissolved in a mixture of dichloromethane (30 mL) and acetonitrile (5 mL). An acetonitrile solution (3 mL) of anhydrous Me_3NO (4.3 mg, 0.057 mmol) was added dropwise at room temperature. After evaporation of the solvent *in vacuo*, the residue was dissolved in chlorobenzene (5 mL). The solution was added dropwise to a refluxing chlorobenzene solution of C_{60} (20.0 mg, 0.0278 mmol, 0.5 equiv), and the reaction mixture was stirred for 90 min. The solvent was evaporated, and the residue was purified by preparative TLC (CS_2) to give compound **7** (6.2 mg, 0.00390 mmol, 14%, $R_f = 0.5$) as a black solid. IR (CS_2) ν(CO) 2064 (vs), 2032 (s), 2010 (s), 1998 (m), 1984 (m), 1960 (w), 1946(w) cm^{-1}; ^1H NMR (CS_2/C_6D_6, 298 K) δ 1.71 (d, $^2J_{PH} = 10.0$ Hz, 9H); $^{31}P\{^1H\}$ NMR (CS_2/C_6D_6, 298 K) δ −47.4 (s); ^{13}C NMR ($C_6D_4Cl_2$, 298 K) δ 185.4 (d, $^2J_{PC} = 5.9$ Hz, 2 CO), 178.5 (s, 6 CO); MS (FAB^+) *m/z* 1596 (M^+). Anal. Calcd for $C_{71}H_9O_8POs_3$:C, 53.59; H, 0.57. Found: C, 53.14; H, 0.38.

Conversion of 6 to 7. Method 1: Compound **6** (20.0 mg, 0.0130 mmol) was dissolved in chlorobenzene (20 mL), and an excess amount (0.006 mL, 0.06 mmol) of PMe_3 was added. The resulting mixture was heated to reflux for 5 h. The solvent was evaporated, and the residue was purified by preparative TLC (CS_2) to afford compound **7** (8.8 mg, 0.0055 mmol, 43%). **Method 2:** Compound **6** (20.0 mg, 0.0130 mmol) was dissolved in chlorobenzene (20 mL), and an excess amount of PMe_3 was added. The solution was cooled to −20 °C, and an acetonitrile solution (3 mL) of anhydrous Me_3NO (1.0 mg, 0.013 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature for 1 h. The solvent was evaporated, and the residue was purified by preparative TLC (CS_2) to afford compound **7** (19.8 mg, 0.0124 mmol, 96%).

X-ray Structure Determination for $1\cdot CH_2Cl_2$. Crystals of **1** suitable for an X-ray analysis were obtained by slow recrystallization from a mixed solvent of toluene, dichloromethane, and hexane at −20 °C. An opaque dark crystal with approximate dimensions of 0.26 × 0.40 × 0.03 mm was mounted and aligned on a CAD4 diffractometer. Details of the relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 25 reflections with $11.39° < \theta < 13.91°$, and intensity data for 4054 independent reflections in the range $0 \le h \le 17$, $0 \le k \le 15$, $0 \le l \le 32$ were collected using graphite-monochromated Mo Kα radiation and the $\omega/2\theta$ scan mode, ω-scan width = $(0.8 + 0.35 \tan \theta)°$, $\theta_{max} = 25°$. One orientation reflection was checked every 300 reflections, and three standard reflections were monitored every 3 h. The intensity variation was less than 1.4% during data collection, and thus, the decay correction was not applied to the data. All data were corrected for *Lp* and absorption factors: the maximum and minimum transmission factors were 1.00 and 0.65 with an average of 0.83. Data collection, cell refinement, and data reduction were performed by SDP.[15] Consistent with the observed values of the cell parameters and observed symmetries in reflection intensities, the unit cell was determined to be orthorhombic. The observed extinctions ($0kl$, $k + l$ = odd; and $hk0$, h = odd) permitted only two space groups; the noncentrosymmetric

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(15) *Structure Determination Package*; Enraf-Nonius: The Netherlands, 1985.

Table 1. Crystal and Structure Determination Data for $1\cdot CH_2Cl_2$

formula	$C_{71}O_{11}Os_3\cdot CH_2Cl_2$
fw	1684.31
cryst syst	orthorhombic
space group	*Pnma*
a, Å	13.879(2)
b, Å	12.034(1)
c, Å	27.468(2)
V, Å^3	4587.7(8)
Z	4
D_{calcd}, Mg m^{-3}	2.439
temp, K	294
λ (Mo Kα), Å	0.710 69
μ, mm^{-1}	8.55
transmission factors	0.65−1.00
no. of rflns measd	5449
no. of unique rflns	4054
no. of rflns ($F_o > 4\sigma(F_o)$)	2885
R_f[a]	0.064
R_w[b]	0.154

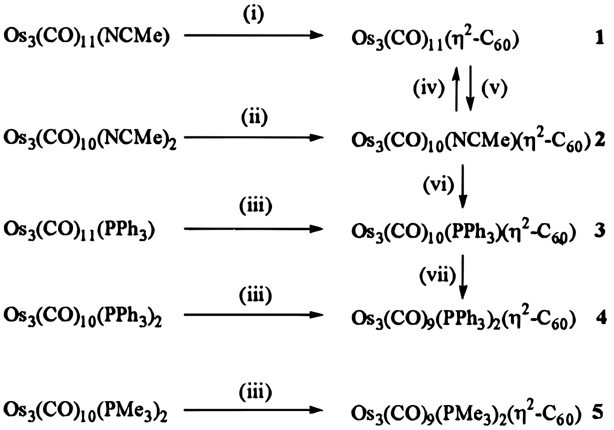
[a] $R_f = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

group $Pna2_1$ (No. 33) and the centrosymmetric group *Pnma* (No. 62).[16] Both possible assignments were tested. Whereas least-squares refinement was processed well in *Pnma*, no satisfactory refinement was obtained in $Pna2_1$ (indeed, unsatisfactory thermal parameters and geometric parameters and high R values were consistently observed in this case). Thus *Pnma* is strongly indicated as a space group for **1**. The structure was determined using the direct-method procedure of the SHELX86 program,[17] which revealed one osmium atom occupied a special position (4c) of space group *Pnma*. The other two osmium atoms, which are at the general position, are disordered at two positions, related by a (x, $^1/_4$, z) mirror plane, with half-occupancy (see Supporting Information). The rest of the atoms in **1** were located from difference Fourier maps. The crystallographic mirror plane passes through the molecule so that six atoms of the three carbonyl groups, four atoms of the C_{60} ligand, and the carbon and one chlorine atom of the CH_2Cl_2 solvate molecule are located on the mirror plane. Six carbonyl groups of the $Os_3(CO)_{11}$ moiety are disordered at the opposite side of the mirror plane with half-occupancy. The chlorine atom located on the mirror plane is split into two positions with an occupancy factor of 0.25, while the other chlorine atom occupies two general positions related by the mirror plane with half-occupancy. The whole structure was refined by full-matrix least-squares techniques on F^2. Of the 58 atoms present in the asymmetric unit, 46 were refined with anisotropic thermal parameters and the remaining 12 atoms were given isotropic thermal parameters (see Supporting Information). For all computations, the SHELX93 package[18] was used and the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, with $\omega = 1/[\sigma^2(F_o^2) + (0.1123P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Neutral atomic scattering factors were used with Os (f′ and f″), corrected for anomalous dispersion. The number of parameters refined was 431. Hydrogen atoms for the CH_2Cl_2 solvate molecule were not located. Final reliability factors for 2885 unique observed reflections [$F_o > 4\sigma(F_o)$] were $R_F = 0.064$, $R_w = 0.154$, with $(\Delta/\sigma)_{max} = 0.102$, $\Delta\rho_{max}/\Delta\rho_{min} = 2.434/-1.301$ e/Å^3 in final $\Delta\rho$ map and $S = 0.982$.

Results and Discussion

Synthesis and Characterization of η^2-C_{60} Complexes 1−5. Details of the reaction conditions for the synthesis of **1**−**5** are summarized in Scheme 1. Oxidative decarbonylation by Me_3NO in the presence of the weak-field ligand MeCN has been used extensively in the activation of $Os_3(CO)_{12}$ and affords the labile derivatives $Os_3(CO)_{12-n}(NCMe)_n$ ($n = 1, 2$), which are versatile starting materials for the synthesis of many triosmium cluster complexes.[12,13] Complexes **1** and **2** have been prepared upon brief heating (5 min for **1**, 30 min for **2**) of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ with C_{60} in toluene at 80 °C, respectively, by substitution of a weakly coordinated MeCN ligand with C_{60}. Longer periods of heating resulted in extensive decomposition and gave lower yields for both **1** and **2**. The phosphine-substituted complexes, **3**−**5**, have been prepared after initial treatment of the corresponding starting material with Me_3NO/MeCN reagent and subsequent reaction with C_{60} at room temperature. Complexes **1** and **2** are interconvertible either by decarbonylation of **1** with Me_3NO/MeCN reagent or by exposure of **2** to CO gas (1 atm). Complex **2** reacts with PPh_3 to afford **3**, which undergoes further reaction with PPh_3 to produce **4** upon decarbonylation with Me_3NO. All these transformations ($1 \rightleftharpoons 2 \rightarrow 3 \rightarrow 4$) proceed in quantitative yields.

Scheme 1. Synthesis of η^2-C_{60} Complexes[a]



[a] Reagents and conditions : (i) C_{60}, toluene, 80 °C, 5 min; (ii) C_{60}, toluene, 80 °C, 30 min; (iii) Me_3NO (1 equiv) / MeCN, CH_2Cl_2, then C_{60}, toluene, room temp., 4 h; (iv) CO (1 atm.), toluene, room temp., 2 h; (v) Me_3NO (1 equiv) / MeCN, toluene, -50 °C, 2 h; (vi) PPh_3 (1 equiv), toluene, room temp., 1 h; (vii) PPh_3 (1 equiv), toluene, then Me_3NO (1 equiv), CH_2Cl_2, -50 °C, 2 h.

Complexes **2**−**5** are soluble in dichloromethane and **1**−**5** in aromatic solvents to form either brown (**1**) or green (**2**−**5**) solutions, but they are insoluble in pentane and hexane. The formulations of **1**−**5** are supported by elemental analysis and by the molecular-ion (M^+) multiplet in the FAB^+ mass spectrum (MS) of each compound. The M^+ multiplet of **1**−**5** perfectly matches the calculated pattern (the highest peak in the M^+ multiplet (m/z, found, calcd), **1** (1600, 1600), **2** (1613, 1613), **3** (1834, 1834), **4** (2068, 2068), and **5** (1696, 1696)). The presence of MeCN ligand in **2** was confirmed by observation of the highest peak at 1616 (**2** + 3) in the MS of the deuterated derivative of **2**, $Os_3(CO)_{10}(CD_3CN)(\eta^2$-$C_{60})$.

The definitive structural assignment of **1**−**5** (see Chart 1) is made on the basis of spectroscopic data (^1H and ^{13}C NMR and IR). The IR spectrum of **1** is identical

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(16) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. A.

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to that of $Os_3(CO)_{11}(PPh_3)$,[19] and the IR spectra of **3** and **4** (**5**) are similar to those of $Os_3(CO)_{10}(PPh_3)_2$[20] and $Os_3(CO)_9(PPh_3)_3$,[21] except that the IR bands of C_{60} complexes are shifted to higher energies by *ca.* 20 cm^{-1} compared to those of the corresponding phosphine derivative, reflecting the electron-withdrawing nature of the C_{60} ligand. Phosphine substitution for CO in $Os_3(CO)_{12}$ invariably occurs at an equatorial site.[22] These results indicate that compounds **1**, **3**, and **4** (**5**) are isostructural with the respective phosphine-substituted complex, $Os_3(CO)_{12-n}(PPh_3)_n$ ($n = 1-3$), and thus the C_{60} moiety occupies an equatorial site as shown in Chart 1. Furthermore, the limiting low-temperature ^{13}C NMR (CO region) of **1*** (*ca.* 50% ^{13}CO-enriched) reveals eight resonances at δ 183.3, 182.9, 181.7, 172.0, 171.9, 170.3, 168.8, and 168.5 with an intensity ratio of 2:2:2:1:1:1:1:1. The three lower-field resonances with higher intensities are considered to be due to three sets of the six axial carbonyl ligands, and the rest of the resonances are attributed to the five inequivalent equatorial carbonyl ligands.[23] These data are entirely consistent with the crystal structure of **1** (*vide infra*), with η^2-C_{60} occupying an equatorial position at an osmium center. The ^{13}C signals for the C_{60} moiety are too weak to be detected. The ^1H NMR spectrum of **2** shows two singlets due to the coordinated MeCN at δ 3.02 (**2a**) and 2.85 (**2b**) in a ratio of 2:1, indicating that **2** exists as two isomers. Upon addition of CD_3CN, the two resonances for **2a** and **2b** slowly (2 h) lose intensity at room temperature and are replaced by a sharp singlet at δ 1.98 due to free MeCN, which is consistent with facile displacement of the coordinated MeCN by the deuterated solvent. In compound **2**, the MeCN ligand may be coordinated at an axial site of an osmium atom, as shown in all known acetonitrile derivatives of triosmium clusters.[24] The limiting low-temperature ^{13}C NMR (CO region) of **2*** shows two sets of 10 resonances due to **2a** and **2b** in an intensity ratio of 2:1. Major isomer **2a** is considered to have a structure with an axial MeCN and a bulky equatorial C_{60} ligand coordinated at the same osmium atom, which is strongly supported by both the crystal structure of $Os_3(CO)_{10}(NCMe)(dmfu)$ (**8**) (dmfu = $MeO_2C(H)C{=}C(H)CO_2Me$)[25] and the fluxional behavior of **2a** (*vide infra*). The dimethylfumarate ligand is known to have a similar electron-withdrawing property to that of C_{60}.[6j] The crystal structure of an isomer obtained from an isomeric mixture of **8** indicated that the axial MeCN and equatorial dmfu ligands were coordinated at the same metal center,[25] which was assumed to be isostructural with **2a**. The only structural possibility of minor isomer **2b** is a structure that axial MeCN and equatorial C_{60} ligands are bonded to each adjacent osmium atom. This structure may produce two isomers due to two inequivalent equatorial sites for C_{60}. We, however, observed only one isomer for **2b** in both the ^1H and ^{13}C NMR spectra (down to 193 K), which may be explained by a fast exchange of the C_{60} ligand between the two inequivalent equatorial sites in the temperature range. It seems that the electron-withdrawing nature of the C_{60} ligand favors the structure of **2a**, which has C_{60} and the donor MeCN ligands bonded to the same metal center, and also accounts for the observation that the methyl proton resonance of **2a** (δ 3.02) is more downfield than that of **2b** (δ 2.85).

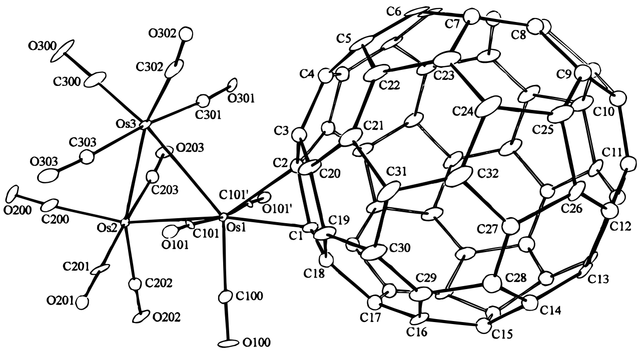

Figure 1. Molecular geometry and atomic-labeling scheme for **1**. Labels for primed atoms of C_{60} are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Esd's for 1·CH_2Cl_2

(A) Metal−Metal Distances			
Os(1)−Os(2)	2.891(1)	Os(1)−Os(3)	2.897(1)
(1)Os(2)−Os(3)	2.851(2)		
(B) Metal−Carbon (Carbonyl) Distances			
Os(1)−C(100)	1.89(2)	Os(1)−C(101)	1.94(1)
Os(1)−C(200)	1.97(3)	Os(2)−C(201)	1.86
Os(2)−C(202)	1.93(5)	Os(2)−C(203)	1.94(4)
Os(3)−C(300)	1.93(3)	Os(3)−C(301)	1.96(3)
Os(3)−C(302)	1.93(3)	Os(3)−C(303)	1.99(3)
(C) Carbon−Oxygen (Carbonyl) Distances			
C(100)−O(100)	1.12(3)	C(101)−O(101)	1.13(2)
C(100)−O(200)	1.14(3)	C(201)−O(201)	1.24(4)
C(202)−O(202)	1.16(6)	C(203)−O(203)	1.17(4)
C(300)−O(300)	1.11(3)	C(301)−O(301)	1.11(4)
C(302)−O(302)	1.13(4)	C(303)−O(303)	1.10(3)
(D) Metal−Carbon (C_{60}) Distances			
Os(1)−C(1)	2.21(2)	Os(1)−C(2)	2.26(2)
(E) Distances within the C_{60} Ligand			
C(1)−C(2)	1.42(3)	C(1)−C(18)	1.45(2)
C(2)−C(3)	1.48(2)	C(10)−C(11)	1.36(3)

Crystal Structure of 1·CH_2Cl_2. The crystal contains a disordered arrangement of discrete $Os_3(CO)_{11}(\eta^2$-$C_{60})\cdot CH_2Cl_2$ molecules, which are mutually separated by normal van der Waals distances. The CH_2Cl_2 solvate molecule does not enter into any significant interactions with molecule **1**. The overall molecular geometry and the atomic-labeling scheme are illustrated in Figure 1. Interatomic distances and angles are listed in Tables 2 and 3, respectively.

The molecular structure of **1** is derived from that of $Os_3(CO)_{12}$ by replacing an equatorial carbonyl group on the Os(1) atom with the C_{60} ligand. The two osmium atoms (2, 3) and six carbonyl ligands (201, 202, 203, 301, 302, 303), however, are disordered out of the crystallographic mirror plane, which includes the Os(1) atom, four C_{60} carbon (1, 2, 10, 11) atoms, and three equatorial carbonyl (100, 200, 300) groups, and bisects the C_{60} ligand and the Os(2)−Os(3) bond. The primed atoms

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Table 3. Selected Interatomic Angles (deg) and Esd's for $1\cdot CH_2Cl_2$

(A) Intermetallic Angles			
Os(1)−Os(2)−Os(3)	59.03(4)	Os(1)−Os(2)−Os(3)	60.59(4)
(B) M−M−CO Angles			
Os(2)−Os(1)−C(100)	123.8(8)	Os(3)−Os(1)−C(100)	139.0(6)
Os(2)−Os(1)−C(101)	89.8(5)	Os(3)−Os(1)−C(101)	77.7(4)
Os(1)−Os(2)−C(200)	149.7(6)	Os(3)−Os(2)−C(200)	92.9(8)
Os(1)−Os(2)−C(201)	78(1)	Os(3)−Os(2)−C(201)	94(1)
Os(1)−Os(2)−C(202)	103(1)	Os(3)−Os(2)−C(202)	161(1)
Os(1)−Os(2)−C(203)	95(1)	Os(3)−Os(2)−C(203)	81(1)
Os(1)−Os(3)−C(300)	152.4(5)	Os(2)−Os(3)−C(300)	97.5(9)
Os(1)−Os(3)−C(301)	79.4(9)	Os(2)−Os(3)−C(301)	96(1)
Os(1)−Os(3)−C(302)	3(9)	Os(2)−Os(3)−C(302)	160.5(9)
Os(1)−Os(3)−C(303)	96.0(9)	Os(2)−Os(3)−C(303)	81(1)
(C) Os−C−O and C−Os−C Angles			
Os(1)−C(100)−O(100)	171(2)	Os(1)−C(101)−O(101)	176(1)
Os(2)−C(200)−O(200)	165(1)	Os(2)−C(201)−O(201)	169(4)
Os(2)−C(202)−O(202)	177(3)	Os(2)−C(203)−O(203)	173(3)
Os(3)−C(300)−O(300)	166(1)	Os(3)−C(301)−O(301)	177(3)
Os(3)−C(302)−O(302)	171(3)	Os(3)−C(303)−O(303)	175(3)
C(100)−Os(1)−C(101)	92.7(4)	C(200)−Os(2)−C(201)	91(1)
C(200)−Os(2)−C(202)	105(1)	C(200)−Os(2)−C(203)	95(1)
C(201)−Os(2)−C(202)	91(1)	C(201)−Os(2)−C(203)	172(2)
C(202)−Os(2)−C(203)	92(1)	C(300)−Os(3)−C(301)	88(1)
C(300)−Os(3)−C(302)	102(1)	C(300)−Os(3)−C(303)	97(1)
C(301)−Os(3)−C(302)	89(1)	C(301)−Os(3)−C(303)	175(1)
C(302)−Os(3)−C(303)	93(1)		
(D) Angles Involving C(1) and C(2)			
C(1)−Os(1)−C(2)	37.1(7)	Os(1)−C(1)−C(2)	73(1)
Os(2)−Os(1)−C(1)	166.6(3)	Os(2)−Os(1)−C(2)	151.2(4)
Os(3)−Os(1)−C(1)	132.7(4)	Os(3)−Os(1)−C(2)	96.3(5)
Os(1)−C(1)−C(18)	121.1(9)	Os(1)−C(2)−C(3)	91(1)
C(18)−C(1)−C(2)	119(1)	C(3)−C(2)−C(1)	122(1)
C(18)−C(1)−C(18)′	103(2)	C(3)−C(2)−C(3)′	104(2)

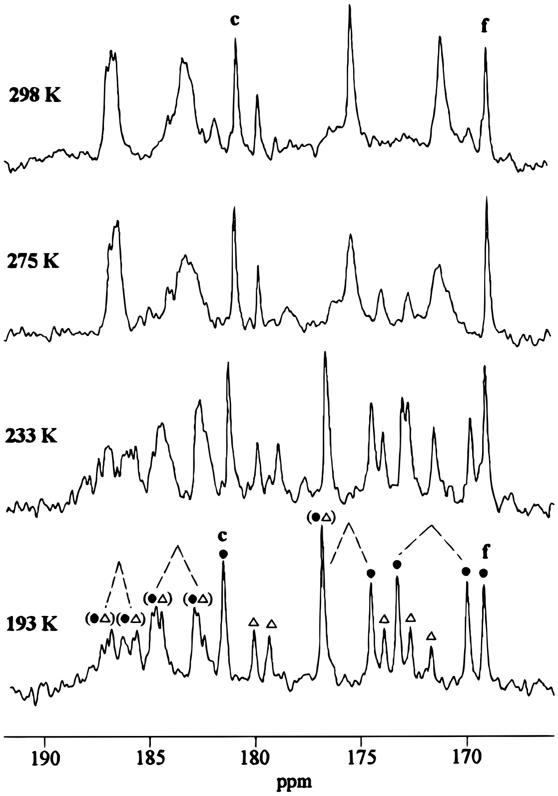

Figure 2. VT ^{13}C NMR spectra (75 MHz, CO region, CD_2Cl_2) of **2***. Resonances marked with ● are from **2a** and those with △ are from **2b**.

are the symmetry mates of the unprimed atoms, and each mate occupies the opposite side of the mirror plane with half-occupancy. The Os(2)−Os(3) bond in the Os_3 triangle is slightly shorter (*ca.* 0.05 Å) than the other two Os−Os bonds. The average Os−Os distance for **1** (2.879(1) Å) is similar to that for $Os_3(CO)_{12}$ (2.877(3) Å).[26] The C_{60} moiety is bound to the Os(1) atom in an η^2 fashion through a 6−6 ring fusion, as found in other η^2-C_{60} transition metal complexes.[6] The dihedral angle between Os(1)−C(1)−C(2) and Os_3 triangles is 19(1)°, and the carbonyl ligands on each osmium atom also reveal significant distortion. Both distortions are, presumably, due to a steric conjestion between the C_{60} and the adjacent equatorial carbonyl (302) ligand. The Os−C(C_{60}) bond distances are Os(1)−C(1) = 2.21(2) Å and Os(1)−C(2) = 2.26(2) Å, which are comparable to the values (2.15(3), 2.22(3) Å) of Os−C(alkene) bonds found in $Os_3(CO)_{10}(PEt_3)[CF_3(H)C{=}C(H)CF_3]$.[27] The C(1)−C(2) bond length is 1.42(2) Å, and this bond is elongated due to the metal-to-C_{60} π-back-donation compared with 1.38(2) Å for an unperturbed (6, 6)-bond. We note here that the following C−C distances of C_{60} directly bonded to the metal center have been observed in η^2-C_{60} complexes: 1.45(3) Å in $Pd(PPh_3)_2(\eta^2\text{-}C_{60})$,[6f] 1.48(1) Å in $RhH(CO)(PPh_3)_2(\eta^2\text{-}C_{60})$,[6e] 1.49(2) Å in $\{Ir(CO)Cl(PEt_3)_2\}_2C_{60}$,[6h] 1.50(1) Å in $W(CO)_3(diphos)(\eta^2\text{-}C_{60})$,[6j] 1.50(3) Å in $Pt(PPh_3)_2(\eta^2\text{-}C_{60})$,[5] 1.51(2) Å in $\{Ir(CO)Cl(PMe_3)_2\}_2C_{60}$,[6h] and 1.53(3) Å in $Ir(CO)Cl(PPh_3)_2(\eta^2\text{-}C_{60})$.[6a] The C(1)−C(2) bond of **1**, therefore, is the shortest value observed in these complexes, implying that the π-back-donation in **1** may be significantly suppressed by strong π-acid carbonyl ligands on the osmium atoms. The C_{60} moiety shows the same distortion of pulling the C(1) and C(2) atoms away from the C_{60} surface as that seen in other complexes: the angles between the C(1) and C(2) axis and the planes described by C(2)−C(3)−C(3)′ and C(1)−C(18)−C(18)′ are 40(2)° and 39(2)°, respectively, but such angles in free C_{60} are known to be 31°.[1b]

All other features of the molecular geometry are within the expected range. The average C−C bond 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 1.38(2) Å. Individual Os−CO distances range from 1.86(3) to 1.99(3) Å, C−O bond lengths range from 1.10(3) to 1.24(4) Å, and Os−C−O angles are in the range 165(1)−177(3)°.

Fluxional Processes of 2 and 5. The molecular dynamics of **2** and **5** have been examined by variable-temperature (VT) ^{13}C NMR spectroscopy using *CO-enriched samples, **2*** and **5***. The limiting low-temperature ^{13}C NMR spectrum of **2*** at 193 K (Figure 2, CO region) reveals two sets of 10 resonances attributed to unsymmetrical structures of **2a** (denoted as ●) and **2b** (△) in an intensity ratio of 2:1. Superimposed [AB] patterns for the eight inequivalent *trans* axial carbonyls for **2a** and **2b** are observed in the range of *ca.* 187−183 ppm, which is consistent with earlier observations that the resonances of axial carbonyls appear at lower field than those of equatorial carbonyls.[28] The carbonyl

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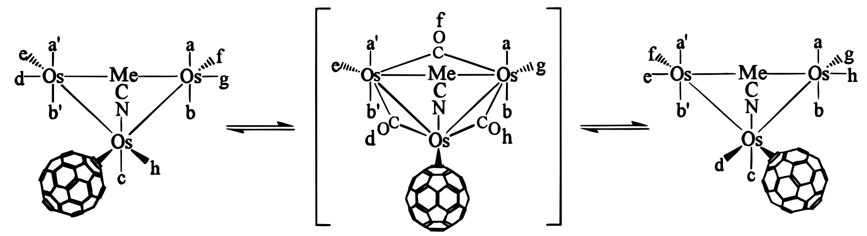
Scheme 2



I (C_s)

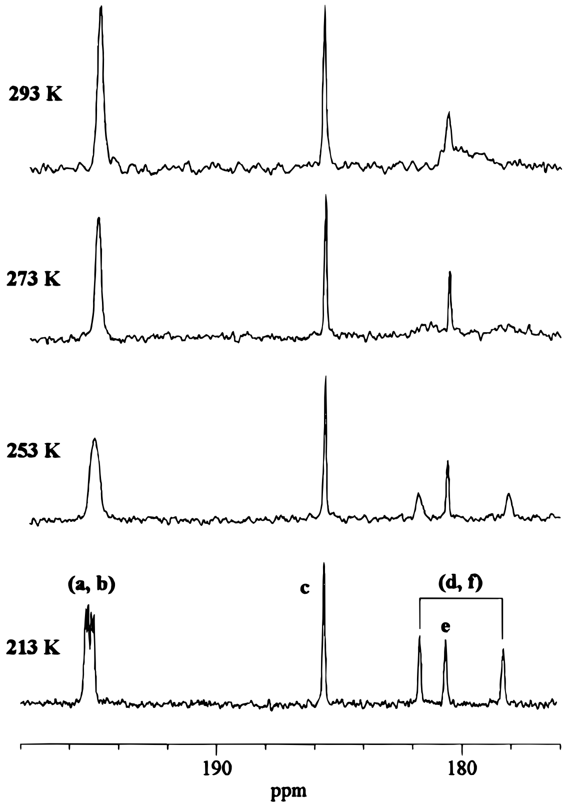


Figure 3. VT ^{13}C NMR spectra (75 MHz, CO region, CD_2Cl_2) of **5***.

equilibration in **2a** is clearly observable between 193 and 298 K. As shown in the spectrum at 298 K, the four complex axial carbonyl resonances become two resonances, the two pairs (δ 176.9, 174.6 and 173.3, 170.0) of equatorial carbonyls are averaged and the two carbonyl signals (δ 181.6, 169.2) are unaffected.

These spectral changes can be interpreted in terms of restricted in-plane cyclic motions of equatorial C_{60} and carbonyl ligands, as shown in Scheme 2. Three equatorial carbonyls (d, f, and h) swing into bridging positions and move on to new osmium atoms and reform the all-terminal carbonyl structure, while the C_{60} ligand swings to the adjacent equatorial site on the same metal atom. This process generates a triply bridged C_s-symmetric intermediate (see I in Scheme 2) and thus leads to pairwise equilibration of the four axial carbonyls a/a′ and b/b′ and the four equatorial carbonyls d/h and e/g. However, axial carbonyl c and equatorial carbonyl f on the mirror plane of the intermediate are not affected by this rearrangement. Equatorial carbonyl f retains its trans relationship through the Os−Os bond to the equatorial C_{60} ligand even after the rearrangement. Therefore, the unique axial carbonyl c is assigned to the next lowest signal at δ 181.6, and the equatorial carbonyl f is assigned to the unaffected higher field resonance at δ 169.2. The free energy of activation ($\Delta G_c^{\ddagger} = 12.7 \pm 0.1$ kcal/mol) has been obtained[29] from a coalescence of the two carbonyl resonances (δ 176.9 and 174.6) at 273 K for the fluxional process of **2a**. A similar fluxional process has been previously observed for the norbonadiene complex $Os_3(CO)_{10}(\eta^2,\eta^2\text{-}C_7H_8)$ with an axial−equatorial-substituted structure ($\Delta G^{\ddagger} = 9.7$ kcal/mol).[30] The solution dynamics of minor isomer **2b** could not be interpreted because of relatively low-intensity signals and overlap of the **2b** resonances with **2a** resonances.

The restricted equilibration of in-plane equatorial C_{60} and carbonyl ligands via a triply bridged intermediate for **2a** is further supported by the solution-dynamics studies on **5**. The VT ^{13}C NMR spectra of **5*** are illustrated in Figure 3. The limiting low-temperature spectrum at 213 K reveals six carbonyl resonances at δ 194.8 ($^2J_{CP} = 7.2$ Hz), 194.5 ($^2J_{CP} = 8.1$ Hz), 185.4, 181.6, 180.6, and 178.3 with relative intensities of 2:2:2:1:1:1, which is consistent with the structure of a pseudo-C_3-symmetry shown in Scheme 3. The two lowest field resonances with C−P couplings and an intensity of 2 are assigned to the two pairs of axial carbonyls, a and b, on the two osmium atoms coordinated with phosphine ligands.[23] The resonance at δ 185.4 with an intensity of 2 is assigned to the two equivalent axial carbonyls, c, on the osmium atom coordinated with the C_{60} ligand. The remaining three resonances with intensities of 1 are due to three inequivalent carbonyls, d, e, and f. As the temperature increases, the two low-field doublets at δ 194.8 and 194.5 broaden and merge into a single peak and the two high-field resonances at δ 181.6 and 178.3 broaden and coalesce at 298 K while the two resonances at δ 185.4 and 180.6 are virtually unaffected. These observations can also be rationalized by the same fluxional process as that for **2a**. The process, via a C_{2v} intermediate shown in Scheme 3, leads to pairwise equilibration among the four axial carbonyls a/b and between the equatorial carbonyls d/f. However, the two axial carbonyls c and the equatorial carbonyl e are not affected by the process. Note that the two inequivalent PMe_3 ligands become equivalent by the rearrangement. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two resonances

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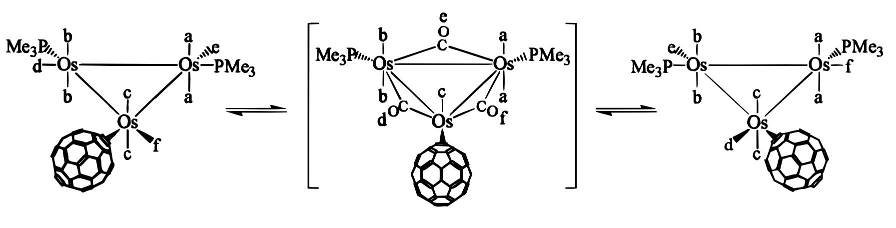
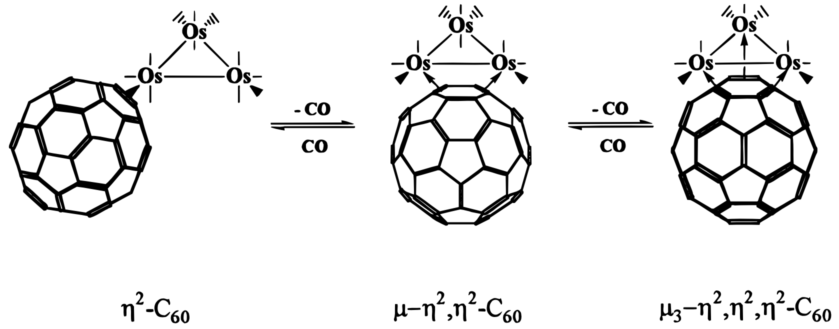
Scheme 3



II (C_{2v})

Scheme 4



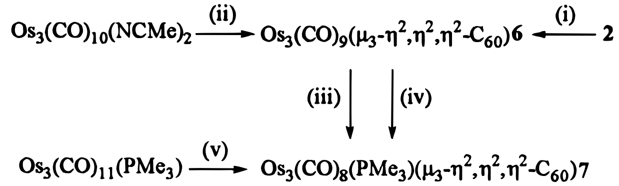
at δ −49.3 and −50.9 at 213 K, which coalesce at 273 K. The line shape analysis[29] of the ^{31}P resonances gives $\Delta G_c^{\ddagger} = 12.7 \pm 0.1$ kcal/mol for the fluxional process of **5**. It is interesting to observe identical $\Delta G_c^{\ddagger}$ values for the similar fluxional processes of **2a** and **5**, strongly suggesting that similar mechanisms operate in both complexes.

We were able to obtain ^{13}C NMR spectrum of the C_{60} moiety with the most soluble complex, **5**, among the C_{60}-triosmium cluster complexes (see Experimental Section). The spectrum at room temperature shows a 17-line C_{2v} symmetry pattern, which can be explained either by the intermediate of C_{2v} symmetry (see II in Scheme 3) for the fluxional process of **5** or by free rotation about the metal−C_{60} bond. Previous studies on fluxional processes of the C_{60} moiety revealed C_{60}−metal bond axis rotation for $M(CO)_4(\eta^2\text{-}C_{60})$ (M = Fe, Ru)[6g] and migration of the metal fragment over the surface of C_{60} for $Pd(PR_3)_2(\eta^2\text{-}C_{60})$ ($R_3 = Me_2Ph, MePh_2, (OMe)_3$)[31] by VT ^{13}C NMR spectroscopy. A recent report by Green and co-workers on $M(NO)(PPh_3)_2(\eta^2\text{-}C_{60})$ (M = Co, Rh)[6k] showed the presence of a C_{60}−metal moiety rotation at low temperatures and a migration process at high temperatures.

Synthesis and Characterization of μ_3-η^2,η^2,η^2-C_{60} Complexes, 6 and 7. We are interested in reversible interconversions of η^2-C_{60}, μ-η^2,η^2-C_{60}, and μ_3-η^2,η^2,η^2-C_{60} ligands on a triosmium cluster framework (see Scheme 4). Successive loss of a carbonyl ligand from η^2-C_{60} complex will give μ-η^2,η^2-C_{60} and μ_3-η^2,η^2,η^2-C_{60} complexes in turn, and the corresponding reverse pathways may render reversibility to these reactions.

Thermolysis of **2** in refluxing toluene (110 °C) has been attempted to prepare a μ-η^2,η^2-C_{60} complex by removing the weak-field MeCN ligand. The reaction resulted in extensive decomposition of **2** and did not produce any isolable products. However, thermolysis of **2** at a higher temperature in refluxing chlorobenzene (134 °C) unexpectedly affords $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**6**) in 23% yield by loss of both the acetonitrile and a carbonyl ligand (see Scheme 5). A better yield (32%) has been obtained from an alternative reaction of $Os_3(CO)_{10}(NCMe)_2$ (2 equiv) and C_{60} (1 equiv). The reaction of **6** with either CO (1 atm) or PMe_3 has been carried out in refluxing chlorobenzene to prepare a μ-η^2,η^2-C_{60} complex by addition of a 2-electron-donor ligand to **6**. The former reaction gives only the starting material back, but the latter reaction produces $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (**7**) in 43% yield by substitution of a carbonyl ligand with PMe_3 instead of the expected addition of PMe_3 to **6**. Complex **7** can be prepared either in a quantitative yield by initial decarbonylation of **6** with Me_3NO/MeCN reagent under mild conditions (−20 °C to room temperature) or in 14% yield by a similar decarbonylation of $Os_3(CO)_{11}(PMe_3)$ (2 equiv) and subsequent thermolysis with C_{60} (1 equiv) in refluxing chlorobenzene. We have not been successful in the preparation of the μ-η^2,η^2-C_{60} complex as of yet.

Scheme 5. Synthesis of μ_3-η^2,η^2,η^2-C_{60} Complexes[a]



[a] Reagents and conditions : (i) CB reflux, 23%; (ii) C_{60} (0.5 equiv), chlorobenzene (CB) reflux (134 °C), 32% yield; (iii) PMe_3, CB reflux, 43%; (iv) CB, PMe_3, Me_3NO (1 equiv) / MeCN at -20 °C, room temp., quantitative. (v) Me_3NO(1 equiv) / MeCN, C_{60} (0.5 equiv), CB reflux, 14%.

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Table 4. Comparison of IR Spectra between μ_3-η^2,η^2,η^2-C_{60} and Arene Complexes

complex	ν_{CO} (cm^{-1})	solvent	ref
$Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$	2078s, 2045vs, 2012m, 1985sh	CS_2	9
$Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$	2071m, 2027vs, 1996s, 1976sh	CH_2Cl_2	32
$Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, **6**	2081s, 2046vs, 2016m, 2002m, 1983sh	CS_2	this work
$Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$	2076m, 2030vs, 1999m, 1978m, 1951sh	CH_2Cl_2	33
$Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, **7**	2064vs, 2032s, 2010s, 1998m, 1984m, 1960w, 1946w	CS_2	this work
$Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$	2057s, 2018vs, 1991s, 1975m, 1962sh, 1943w, 1920w	CH_2Cl_2	33

Complexes **6** and **7** are sparingly soluble in toluene and more soluble in carbon disulfide and 1,2-dichlorobenzene to form either a brown (**6**) or greenish-brown (**7**) solution. Formulations of both complexes are established by elemental analysis and by FAB$^+$ MS spectroscopy. The M$^+$ multiplet of **6** and **7** completely matches the calculated pattern: the highest peaks in the M$^+$ multiplet (*m*/*z*, found, calcd) for **6** are 1544, 1544 and **7** are 1592, 1592. The carbonyl regions of the IR spectra for **6** and **7** are similar in pattern to those reported for face-capping arene complexes,[33] $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$ and $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$ (see Table 4), whose structures are derived from replacement of three axial carbonyls at a triosmium face and the capping of $\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6$ ligand. Shapley and co-workers recently reported the structural characterization of $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$[9] and $\{Ru_3(CO)_9\}_x(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{70})$ (x = 1, 2),[34] which verify arene-like coordination of the C_{60} ligand to the open face of a triruthenium cluster. An extra band is observed for C_{60} and arene triosmium complexes compared to the corresponding triruthenium complexes, as shown in Table 4. The shift of the IR bands for C_{60} complexes to higher energies is consistently revealed in these complexes due to the electron-withdrawing nature of the C_{60} ligand. The structural correspondence between C_{60} and arene complexes are indicated by the close similarities of the IR spectra.

The ^{13}C NMR spectrum of **6*** at 298 K (Figure 4a) reveals a single resonance at δ 176.1 for the nine carbonyls, which implies the presence of a fast localized 3-fold rotation of three carbonyl groups on each atom. The arene analogue $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$,[33] however, has two resonances at δ 175.86 (6 CO) and 175.82 (3 CO) for the six equatorial and three axial carbonyl ligands, although they are very close in chemical shifts. The single carbonyl resonance of **6*** became slightly broad at 188 K but was not resolved. A single-crystal X-ray diffraction study has previously revealed equatorial coordination of triphenylphosphine in $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$,[33] which appears to be isostructural with compound **7**. The ^{13}C NMR spectrum of **7** at 298 K (Figure 4b) shows two resonances at δ 185.4 (d, $^2J_{PC}$ = 5.9 Hz) and 178.5 in a 1:3 ratio, whose general features are very similar to that of the arene analogue with two peaks at δ 183.96 (d, $^2J_{PC}$ = 8.0 Hz, 2 CO) and 177.39 (s, 6 CO). The P–C coupling in **7** was verified by obtaining a $^{13}C\{^{31}P\}$ NMR spectrum (see the inset of Figure 4). A fast localized 3-fold rotation of three ligands at each osmium center seems to occur in **7** also. The phosphine-substituted osmium center in **7** may undergo a restricted 3-fold rotation proposed by Pomeroy and co-workers,[35] without requiring the bulky phosphine ligand to enter an axial site. In any case, the resonance at δ 185.4 with a P–C coupling and that at δ 178.5 can be assigned to the two carbonyl ligands on the osmium atom coordinated with PMe_3 and the six carbonyl groups on the other two osmium atoms, respectively. The two resonances only become broad at a low temperature of 188 K.

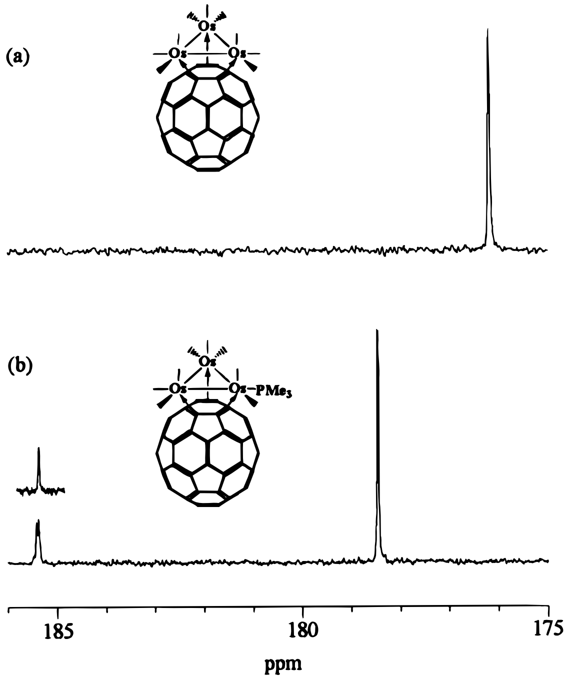

Figure 4. (a) ^{13}C NMR spectrum (151 MHz, CO region, 298 K, CS_2/ext.CD_2Cl_2) of **6***. (b) ^{13}C NMR spectrum (151 MHz, CO region, CS_2/C_6D_6) of **7***. The inset is from the $^{13}C\{^{31}P\}$ NMR spectrum.

Concluding Remarks

The present work provides the first examples of transition metal cluster-bound C_{60} complexes, **1**–**7**, although the only C_{60}–metal cluster complex, $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[9] has appeared in the literature after our preliminary communication.[10] As expected, the C_{60} ligand in **1**–**5** invariably occupies an equatorial position similar to bulky ligands, such as phosphines and alkenes, and acts as an electron-withdrawing entity evidenced by high-energy ν(CO) bands in **1**–**7**. The shortest C–C bond length (1.42 Å in **1**) of C_{60} directly bonded to the metal center among all known η^2-C_{60} complexes, however, implies that the metal-to-C_{60} π-back-donation is significantly suppressed by the strong π-acid carbonyl ligands on the osmium atoms. This fact is further supported by our previous observation[11] that C_{60}-mediated electron transfer to the metal center

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occurs in the electrochemical pathways of **1**, **3**, and **4**. A η^6-C_{60} ligand has only been observed in trimetallic ruthenium and osmium (**6** and **7**) cluster complexes. These results suggest that a metal triangle provides for effective overlap of metal d orbitals with C_{60} p_π-orbitals, which is known to be oriented at angle of *ca.* 10°[36] away from the perpendicular face of the six-membered ring of C_{60}. Nevertheless formation of μ-η^2,η^2-C_{60} complexes eluded our observation. There are three possible fluxional processes proposed for $Os_3(CO)_{12}$ and its derivatives: (1) axial−equatorial ligand exchange between two metal centers through an intermediate like the solid structure of $Fe_3(CO)_{12}$, (2) equatorial ligand exchange among three metal centers via a triply bridged intermediate, and (3) axial−equatorial ligand exchange through a localized 3-fold rotation of ligands on each metal center. Both complexes **2a** and **5** have shown a fluxional process ($\Delta G_c^\ddagger = 12.7 \pm 0.1$ kcal/mol) of the restricted pathway of (2) due to the presence of MeCN and C_{60} ligands, which cannot commonly bridge. Complexes **6** and **7** appear to undergo the fluxional pathway (3) of a facile 3-fold rotation on each osmium atom, even down to a very low temperature (188 K).

Acknowledgment. We are grateful to the Korea Advanced Institute of Science and Technology for financial support of this research.

Supporting Information Available: Figures of disordered molecular geometry and the packing diagram and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and complete bond lengths and angles for complex **1** (11 pages). Ordering information is given on any current masthead page.

OM970689P

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