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ABSTRACT

 $Os_3(CO)_7(1,2-dppm)(\mu_3-\eta^2;\eta^2;\eta^2-C_{60})$ (1) and $Os_3(CO)_7(1,1-dppm)(\mu_3-\eta^2;\eta^2-C_{60})$ (2) were prepared by decarbonylation of $Os_3(CO)_9(\mu_3-\eta^2;\eta^2-C_{60})$ (3) with Me₃NO/MeCN in the presence of excess dppm (bis(diphenylphosphino)methane) in chlorobenzene. Then, compounds 1 and 2 were characterized by obtaining spectroscopic and microanalytical data, as well as by performing single-crystal X-ray diffraction studies. In addition, the electrochemical properties of 1 and 2 were examined by performing cyclic voltammetry. The cyclic voltammograms suggest that a C₆₀-mediated electron transfer to the osmium cluster center takes place for species 1^{3-} and 2^{3-} in compounds 1 and 2.

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Introduction

Since the discovery of fullerene and its synthesis in mass quantities [1], an enormous number of fullerene derivatives have been synthesized and characterized to develop new nanomaterials and nanodevices [2-4]. For example, organic derivatives of fullerene have been extensively used in donor-acceptor bulk heterojunction (BHJ) solar cells as electron-acceptor materials because of their remarkable and adjustable electronic properties and solution processability [5]. Various organic methods have been used for the covalent functionalization of fullerenes, including cyclopropanation [6], 1,3-dipolar cycloaddition [7], and Diels-Alder cycloaddition [8]. However, direct covalent functionalization disturbs the π -conjugation system of fullerene by forming a σ -bond, and thus the prepared fullerene derivatives show rather poorly defined electrochemical properties and instability in reduced states, which severely limits their technological applications. Along with the organic derivatives of fullerene, exohedral metallofullerenes have received much attention regarding the effects of metal coordination on the chemical and physical properties of C_{60} [9–18]. In particular, C_{60} -metal cluster complexes, μ_3 - η^2 : η^2 : η^2 , between the metal-cluster and C₆₀, have robust thermal and electrochemical stabilities as well as strong electronic communication between C₆₀ and the metal cluster centers. Furthermore, the metal cluster $-C_{60}$ bonding mode can be controlled by modifying the coordination sphere of the metal centers, and the electrochemical properties of the C₆₀-metal cluster complexes can be fine-tuned by changing the ligands attached on the metal cluster. Various C₆₀-metal cluster complexes with $\mu_3-\eta^2:\eta^2:\eta^2$ bonding modes have been reported so far [19–27]. In particular, tertiary phosphine ligands have been interesting to organometallic chemists for a long time because of their ability to stabilize a variety of oxidation states of transition metals. The electronic and steric properties of phosphine ligands in the transition metal-complex catalyst can be finely tuned by modifying the substitution group, which influences the rate of the reaction and product selectivity. Moreover, the strong electron-donating ability of the phosphine ligand can alter the electrochemical properties of metal clusters or C₆₀-metal cluster complexes [22]. As part of our continuing interest in fullerene-metal cluster complexes and phosphine ligands, we herein report the synthesis, structure, and electrochemistry of bis(diphenylphosphino)methane-substituted C₆₀-triosmium complexes, $Os_3(CO)_7(1,2-dppm)(\mu_3-\eta^2:\eta^2-C_{60})$ (1) and metastable $Os_3(CO)_7(1,1-dppm)(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ (2).

which include a face-capping cyclohexatriene-like bonding mode,





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Experimental

General comments

All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried over the appropriate drying agents and distilled immediately before use, C_{60} (99.5%, SES Research) and bis(diphenvlphosphino)methane(dppm) (97%, Aldrich) were used without further purification. Anhydrous trimethylamine N-oxide was obtained from Me₃NO·2H₂O (98%, Aldrich) by sublimation (three times) at 90-100 °C under vacuum. $Os_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ (4) [21] was prepared using methods from the literature. Preparative thin-layer chromatography (TLC) plates were prepared with silica gel GF₂₅₄ (Type 60, E. Merck). Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. The ¹H(400 MHz) and ¹³C(100 MHz) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer, and ³¹P(122 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer. Matrix-assisted laser desorption/ionization time-offlight (MALDI-TOF) mass spectra were obtained by the staff of the Korea Basic Science Institute (KBSI), and all m/z values are referenced to ¹⁹²Os. Elemental analyses were performed by the staff of the Energy & Environment Research Center at KAIST.

Preparation of $Os_3(CO)_7(1,2-dppm)(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ (**1**) and $Os_3(CO)_7(1,1-dppm)(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ (**2**)

An acetonitrile solution of anhydrous Me₃NO (1.5 mg, 0.0196 mmol) was added dropwise to a chlorobenzene (CB) solution (20 mL) of Os₃(CO)₉(μ_3 - η^2 : η^2 : η^2 -C₆₀) (**4**) (30 mg, 0.0194 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature for 30 min. After evaporation of the solvent in vacuo, the residue was dissolved in CB (20 mL) containing dppm (30 mg, 0.0780 mmol). The resulting solution was heated at 60 °C for 4 h. Evaporation of the solvent and purification by multiple (three times) preparative TLC elution (CS₂/CH₂Cl₂ = 15:1) produced compound **1** (15 mg, 0.0080 mmol, 41%, $R_f = 0.6$) as a brownish green solid and compound **2** (12 mg, 0.0064 mmol, 33%, $R_f = 0.5$) as a green solid.

Compound 1

IR(CH₂Cl₂): ν_{CO} 2059 (vs), 2007 (vs), 1994 (vs), 1971 (sh), 1932 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.48–7.17 (m, 20H, phenyl), δ 5.55 (dt, 1H, *J*_{HH} = 14.3 Hz, *J*_{PH} = 10.7 Hz, PCH₂P), 4.51 (dt, 1H, *J*_{HH} = 14.4 Hz, *J*_{PH} = 12.6 Hz, PCH₂P); ¹³C NMR (100 MHz, C₆D₄Cl₂, 298 K): carbonyl carbon, δ 192.4 (t, 2CO, *J*_{PC} = 3 Hz), 185.2 (t, 2CO, *J*_{PC} = 2.2 Hz), 178.9 (s, 3CO); C₆₀, δ 158.7 (t, 2C, *J*_{PC} = 1.5 Hz), 157.6 (2C), 154.4 (2C), 152.4 (2C), 145.7 (2C), 145.0 (2C), 144.8 (2C), 144.7 (2C), 146.6 (2C), 144.3 (2C), 144.2 (4C), 144.2 (2C), 143.7 (3C), 143.5 (2C), 143.4 (2C), 143.4 (2C), 142.9 (2C), 142.8 (2C), 142.6 (1C), 142.4 (2C), 142.3 (1C), 61.0 (t, 2C, *J*_{PC} = 1.6 Hz), 61.0 (2C), 59.7 (2C); methylene carbon, C₆₀, δ 39.4 (t, 1C, *J*_{PC} = 34.5 Hz); ³¹P{¹H} NMR (122 MHz, CDCl₃, 298 K): δ –19.4 (s); MS (MALDI-TOF): *m/z*: 1872. Anal. Calcd. for C₉₂H₂₂O₇Os₃P₂: C, 59.04; H, 1.17. Found: C, 58.98; H, 1.16.

Compound 2

IR(CH₂Cl₂): ν_{CO} 2062 (sh), 2054 (vs), 2024 (s), 1986 (s), 1953 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.60–7.14 (m, 20H, phenyl), δ 6.21 (dt, 1H, *J*_{HH} = 14.4 Hz, *J*_{PH} = 10.2 Hz, PCH₂P), 5.15 (dt, 1H, *J*_{HH} = 14.4 Hz, *J*_{PH} = 10.2 Hz, PCH₂P); ¹³C NMR (100 MHz, C₆D₄Cl₂, 298 K): carbonyl carbon, δ 179.7 (6CO), 178.9 (1CO), C₆₀, δ 160.9 (2C), 158.0 (2C), 155.0 (2C), 153.6 (2C), 151.3 (1C), 147.9 (2C), 147.7 (2C), 147.6 (2C), 146.3 (2C), 145.8 (2C), 145.7 (2C), 144.8 (2C),

144.8 (2C), 144.6 (2C), 144.5 (2C), 144.5 (2C), 144.0 (2C), 143.9 (2C), 143.9 (3C), 143.3 (2C), 143.3 (2C), 142.7 (4C), 142.7 (1C), 142.6 (1C), 142.4 (2C), 141.8 (2C), 141.7 (2C), 62.25 (2C), 60.1 (2C), 57.7 (2C); ³¹P {¹H} NMR (122 MHz, CDCl₃, 298 K): δ –45.8 (s); MS (MALDI-TOF): *m/z*: 1872. Anal. Calcd. for C₉₂H₂₂O₇Os₃P₂: C, 59.04; H, 1.17. Found: C, 58.61; H, 1.13.

Conversion of 2 to 1

A CB solution (20 ml) of **2** (20 mg, 0.010 mmol) was heated to reflux for 3 h. Evaporation of the solvent and purification by multiple (three times) preparative TLC elution ($CS_2/CH_2Cl_2 = 15:1$) afforded compound **1** (15 mg, 0.0080 mmol, 75%, $R_f = 0.6$) as a brownish green solid.

X-ray crystallographic studies

Crystals of **1** and **2** suitable for X-ray analysis were grown by slow solvent diffusion of **1** and **2** in hexane into carbon disulfide at room temperature. Diffraction data for **1** and **2** were collected on a Bruker SMART diffractometer/CCD area detector at 273 K and 293 K, respectively. The preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. A hemisphere of reflection data was collected at scan intervals of 0.5° in 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 [28].

Each structure was solved using direct [29] and difference Fourier methods and was refined using the full-matrix leastsquares method based on F^2 (SHELX 97) [30]. All non-hydrogen atoms were refined with anisotropic thermal coefficients. The details of the relevant crystallographic data for **1** and **2** are summarized in Table 1.

Electrochemical measurements

Cyclic voltammetry was carried out on an AUTOLAB (PGSTAT 10, Eco Chemie, Netherlands) electrochemical analyzer using a conventional three-electrode system with a platinum working electrode (1.6 mm diameter disk, Bioanalytical Systems, Inc.), a

 Table 1

 Crystal and structure determination data for 1 and 2.

	1	2
Formula	C ₉₂ H ₂₂ Os ₄ O ₇ P ₂	C ₉₂ H ₂₂ Os ₄ O ₇ P ₂
FW	1871.64	1871.64
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	P21
a, Å	13.722(9)	12.4531(2)
<i>b</i> , Å	24.41(2)	19.3008(4)
<i>c</i> , Å	19.65(1)	13.1552(3)
α, deg	90	90
β , deg	107.16(1)	116.365(1)
γ , deg	90	90
V, Å ³	6288(7)	2833.0(1)
Ζ	4	2
$D_{ m calcd}$, Mg m ⁻³	1.977	2.194
Temp, K	273(2)	293(2)
λ (Mo Kα), Å	0.71073	0.71073
μ , mm ⁻¹	6.166	6.842
$\theta_{\min,\max}$, deg	1.37, 28.24	1.73, 28.38
R _f ^a	0.0578	0.0511
R _w ^b	0.1529	0.0862
GOF	1.015	0.964

^a $R_{\rm f} = \Sigma ||F_{\rm o}| - |F_{\rm c}||/\Sigma |F_{\rm o}|.$

^b $R_{\rm w} = [\Sigma \omega (|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma \omega |F_{\rm o}|^2]^{1/2}.$

platinum wire counter electrode (5 cm length and 0.5 mm diameter), and an Ag/Ag⁺ reference electrode (0.1 M AgNO₃/Ag in acetonitrile with a VycorTM salt bridge). All measurements were performed at ambient temperature under a nitrogen atmosphere in a dry deoxygenated 0.1 M *o*-dichlorobenzene solution of [(*n*-Bu)₄N] ClO₄. The concentrations of the 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 vs. (time)^{-1/2} according to the Cottrell equation [31].

Results and discussion

Synthesis and characterization of 1 and 2

The synthetic procedures for **1** and **2** are summarized in Scheme 1. The initial decarbonylation of $Os_3(CO)_9(\mu_3-\eta^2;\eta^2;\eta^2-C_{60})$ (**3**) with Me₃NO/MeCN and subsequent reaction with dppm in CB at 60 °C gave $Os_3(CO)_7(1,2-dppm)(\mu_3-\eta^2;\eta^2;\eta^2-C_{60})$ (**1**) (41%) and $Os_3(CO)_7(1,1-dppm)(\mu_3-\eta^2;\eta^2:q^2-C_{60})$ (**2**) (33%). Compound **2**, the 1,1-complex, is completely converted to compound **1**, the 1,2-complex, in 75% yield by 3 h of reflux in CB. Compounds **1** and **2** were formulated on the basis of elemental analyses and mass spectroscopic data. The MALDI TOF mass spectra showed molecular ion isotope multiplets at *m/z* 1872 for **1** and **2**.

The ¹H NMR spectra of **1** and **2** exhibit two doublet-of-triplets (dt) patterns in the methylene proton region, which indicates that both phosphine atoms in the dppm ligand coordinate to metal atoms and that the methylene protons are diastereotopic. The ³¹P {¹H} NMR spectra display a singlet at δ –19.4 for **1** and at δ –45.8 for **2** (cf. δ –168.7 for Os₃(CO)₁₀(1,2-dppm)) [32]. The carbonyl region in the ¹³C NMR spectrum of **1** shows three resonances at δ 192.4 (t, 2CO, $J_{PC} = 3$ Hz), 185.2 (t, 2CO, $J_{PC} = 2.2$ Hz), and 178.9 (s, 3CO) in an intensity ratio of 2:2:3 (Fig. 1a). The two low-field triplet resonances at δ 192.4 and 185.2 are due to two axial and two equatorial carbonyls on the osmium centers bound to the dppm ligand. The low-field singlet resonance at 178.9 is due to the three equivalent carbonyls related by a fast 3-fold rotation on the Os(CO)₃ center. On the other hand, the *sp*³ carbon region of **1** shows three resonances at δ 61.0 (t, 2C, $J_{PC} = 1.6$ Hz), 61.0 (2C), and 59.7 (2C) with an



Scheme 1. Synthesis of 1 and 2.



Fig. 1. ¹³C NMR spectrum (100 MHz, *o*-ODCB- d_4 , 298 K) of **1**: (a) carbonyl region and (b) sp^3 carbon region, *CS₂.

intensity ratio of 1:1:1, which are assigned to the six coordinated carbons (Fig. 1b). These observations are consistent with the idealized C_s symmetric nature of **1** in solution. The ¹³C NMR spectrum (carbonyl region) of **2** reveals two resonances at δ 179.7 (6CO) and 178.9 (1CO) (Fig. 2a). The large resonance at δ 179.7 is assigned to the six carbonyl ligands on the two Os(CO)₃ centers of **2** related by 3-fold rotation. Furthermore, the sp^3 carbon region in the ¹³C NMR spectrum of **2** shows three resonances at δ 62.2, 60.1, and 57.7 with an intensity ratio of 1:1:1, as was found for compound **1** (Fig. 2b). The overall shape of the ¹³C NMR spectrum of **2** in solution.

X-ray crystal structures of 1 and 2

Details of the crystallographic data for **1** and **2** are summarized in Table 1, and selected interatomic distances and angles are listed in Tables 2 and 3 for **1** and **2**, respectively. The molecular structures of **1** and **2** are shown in Figs. 3 and 4. The overall structural features of **1** and **2** are similar to those of known osmium cluster fullerene compounds, except for the dppm ligands [22,33]. The average Os– Os distances of **1** (2.911(1) Å) and **2** (2.9085(7) Å) are longer than those for Os₃(CO)₁₂ (2.877(3) Å) [34] and Os₃(CO)₁₀(1,2-dppm) (2.879(1) Å) [35]. A similar trend was also found for



Fig. 2. ¹³C NMR spectrum (100 MHz, *o*-ODCB- d_4 , 298 K) of **2**: (a) carbonyl region and (b) sp^3 carbon region.

Table 2	
Selected interatomic distances (Å) and angles (d	eg) for 1 .

Bond distances			
Os(1)-Os(2)	2.897(1)	Os(1)–Os(3)	2.910(1)
Os(2)-Os(3)	2.927(2)	Os(1)-P(1)	2.317(3)
Os(2)-P(2)	2.335(3)	Os(1)-C(1A)	1.88(1)
Os(1)-C(1B)	1.90(1)	Os(2)-C(2A)	1.90(1)
Os(2)-C(2B)	1.90(1)	Os(3)-C(3A)	1.92(1)
Os(3)-C(3B)	1.87(2)	Os(3)-C(3C)	1.92(1)
Os(1)-C(1)	2.29(1)	Os(1)-C(2)	2.32(1)
Os(2)-C(3)	2.25(1)	Os(2)-C(4)	2.26(1)
Os(3)-C(5)	2.23(1)	Os(3) - C(6)	2.28(1)
C(1) - C(2)	1.44(1)	C(2)-C(3)	1.49(1)
C(3) - C(4)	1.46(1)	C(4)-C(5)	1.48(2)
C(5) - C(6)	1.43(2)	C(1)-C(6)	1.47(1)
Bond angles			
Os(2)-Os(1)-Os(3)	59.96(2)	Os(1) - Os(2) - Os(3)	60.53(4)
Os(1)-Os(3)-Os(2)	59.51(3)	Os(1) - P(1) - C(501)	108.6(4)
P(1)-C(501)-P(2)	119.1(6)	C(501)–P(2)–Os(2)	115.9(4)
P(2)-Os(2)-Os(1)	86.66(7)	Os(2)-Os(1)-P(1)	99.12(7)

Os₃(CO)₈(PPh₃)(μ_3 - η^2 : η^2 : η^2 -C₆₀) [22], in which the triphenyl phosphine ligand is coordinated to one osmium atom in the equatorial position. In compound **1**, the dppm ligand bridges two Os centers, Os1 and Os2 (Os1–P1 = 2.317(3) Å; Os2–P2 = 2.335(3) Å), in the equatorial position. On the other hand, the dppm ligand in **2** is chelated on the Os1 atom (Os1–P1 = 2.333(3) Å; Os1–P2 = 2.327(3) Å) in the equatorial site. The bridged Os1–Os2 distance (2.897(1) Å) in compound **1** is slightly shorter than the non-bridged Os2–Os3 (2.927(2) Å) and Os1–Os3 (2.910(1) Å) distances, which is consistent with the previously reported result for Ru₃(CO)₁₀(μ -dppm) [36]. The Os–CO distances range from 1.87(2) to 1.92(1) Å and from 1.87(1) to 1.92(1) Å for **1** and **2**, respectively.

The C₆₀ ligand in **1** and **2** is coordinated to the Os1–Os2–Os3 triangle in a typical μ_3 - η^2 : η^2 : η^2 -C₆₀ arene-type fashion. The average Os–C(C₆₀) bond distances in **1** and **2** are 2.27(1) and 2.26(1) Å. The C–C bonds in the μ_3 - η^2 : η^2 : η^2 -C₆₀ ligand alternate in length, with average long distances of 1.48(1) Å for **1** and 1.47(2) Å for **2** and average short distances of 1.44(1) Å for **1** and 1.43(2) Å for **2**. The dppm ligand and triosmium cluster form a five-membered Os1–P1–C501–P2–Os2 metallacycle moiety on the cluster. The angles of the five-membered ring in **1** are 108.6(4)° (\angle Os1–P1–C501), 119.1(6)° (\angle P1–C501–P2), 115.9(4)° (\angle C501–P2–Os2), 86.66(7)° (\angle P2–Os2–Os1), and 99.12(7)° (\angle Os2–Os1–P1), which are comparable to those of Os₃(CO)₁₀(1,2-dppm) (111.2(3)°, 117.4(6)°, 112.6(3)°, 89.76(8)°, and 93.86(8)°) [35]. In compound **2**,

Table J			
Selected interatomic di	istances (Å) and	angles (deg) for	2.

Table 2

Bond distances			
Os(1) - Os(2)	2.9199(7)	Os(1) - Os(3)	2.8969(6)
Os(2) - Os(3)	2.9088(7)	Os(1)-P(1)	2.333(3)
Os(1)-P(2)	2.327(3)	Os(1)-C(1A)	1.88(1)
Os(2)-C(2A)	1.90(1)	Os(2)-C(2B)	1.87(1)
Os(2)-C(2C)	1.92(1)	Os(3)-C(3A)	1.90(2)
Os(3)-C(3B)	1.88(1)	Os(3)-C(3C)	1.89(1)
Os(1)-C(1)	2.30(1)	Os(1)-C(2)	2.23(1)
Os(2)-C(3)	2.33(1)	Os(2)-C(4)	2.23(1)
Os(3) - C(5)	2.23(1)	Os(3)-C(6)	2.26(1)
C(1) - C(2)	1.42(2)	C(2)-C(3)	1.47(2)
C(3) - C(4)	1.46(2)	C(4) - C(5)	1.47(2)
C(5) - C(6)	1.42(2)	C(1)-C(6)	1.48(2)
Bond angles			
Os(2) - Os(1) - Os(3)	60.01(2)	Os(1)-Os(2)-Os(3)	59.60(2)
Os(1) - Os(3) - Os(2)	60.34(2)	Os(1) - P(1) - C(501)	95.6(4)
P(1)-C(501)-P(2)	93.5(5)	C(501) - P(2) - Os(1)	94.9(4)
P(2) - Os(1) - P(1)	69.9(1)		



Fig. 3. Molecular structure of 1. Hydrogen atoms are omitted for clarity.

the dppm ligand forms a four-membered Os1–P1–C501–P2 ring. The angles of the four-membered ring are 95.6(4)° (\angle Os1–P1–C501), 93.5(5)° (\angle P1–C501–P2), 94.9(4)° (\angle C501–P2–Os1), and 69.9(1)° (\angle P2–Os1–P1). The \angle P2–Os1–P1 angle in **2** is very acute in comparison with the other angles. Therefore, compound **2** is unstable, with a large angle strain, and is easily converted to compound **1**. All the bond distances and angles for **1** and **2**, including those for the carbonyl and C₆₀ ligands, are within the expected ranges. To our best knowledge, this is first demonstration that dppm chelates the Os site in the triosmium cluster system. The reaction of Os₃(CO)₁₀(MeCN)₂ or Os₃(CO)₁₀(C4H₆) with the dppm ligand usually yields only the bridged product,



Fig. 4. Molecular structure of 2. Hydrogen atoms are omitted for clarity.

 $Os_3(CO)_{10}(1,2-dppm)$ [32,37], because the angle strain in the fourmembered ring of the 1,1-isomer is extremely severe. However, chelating dppm in metal cluster has been observed in Ir₄, Ru₅ cluster system [38,39].

Electrochemical studies of 1 and 2

The electrochemical properties of compounds 1 and 2 in 1,2dichlorobenzene (DCB) have been examined by performing cyclic voltammetry with tetrabutylammonium perchlorate as the supporting electrolyte. Cyclic voltammograms (CVs) of **1** and **2** are shown in Fig. 5. The half-wave potentials $(E_{1/2})$ of all the new compounds together with those of free C_{60} , $Os_3(CO)_8(PMe_3)(\mu_3 - \mu_3)$ $\eta^{2}:\eta^{2}:\eta^{2}-C_{60}$ (4), $Os_{3}(CO)_{7}(PMe_{3})_{2}(\mu_{3}-\eta^{2}:\eta^{2}-C_{60})$ (5) [22], $Os_3(CO)_8(CNCH_2Ph)(\mu_3-\eta^2:\eta^2-C_{60})$ (**6**), and $Os_3(CO)_7(CNCH_2Ph)_2$ $(\mu_3 - \eta^2 : \eta^2 - C_{60})$ (7) [33] are provided in Table 4.

The CVs of 1 and 2 reveal three reversible redox waves in which third redox waves correspond to a two-electron process. The third and fourth redox processes overlap within the DCB solvent potential window. The general features of the CVs of 1 and 2 are similar to those of the previously reported Os₃(CO)₈(PMe₃)(µ₃- $\eta^{2}:\eta^{2}:\eta^{2}-C_{60}$ (4) [22] and Os₃(CO)₇(CNCH₂Ph)₂($\mu_{3}-\eta^{2}:\eta^{2}:\eta^{2}-C_{60}$) (7) [33] complexes, as shown in Table 4. All four half-wave potentials of 1 and 2 appear at potentials at least ca. 30 mV more negative than those of 4. However, the first and second wave potentials of 1 and **2** are similar to those of **7**, even though the third and fourth half-wave potentials are much more negative (by ca. 180 mV). The potentials of 1 and 2 are most similar to those of 5 despite the different CV graphs. The CVs of **1** and **2** are almost the same, but each half-wave potential of **1** appears at a slightly more positive potential (40 mV, 20 mV, and 10 mV) than the corresponding potential of **2**. This result demonstrates that electronic characteristics of compounds **1** and **2** are almost identical. The first through third reduction potentials of 1 (-1.11, -1.45, and -2.02 V) and 2(-1.15, -1.48, and -2.03) show large cathodic shifts compared to those of free C_{60} (-1.08, -1.46, and -1.90 V) because of the donor effect of the dppm ligand, which indicates that compounds 1 and 2 undergo three successive C₆₀-localized reductions. The third and fourth reductions of **1** and **2** take place at the same potential (**1**: 2.02 V; 2: 2.03 V), which is even more positive (1: 360 mV; 2: 350 mV) than the fourth reduction of free C₆₀ at 2.38 V. The overlap of the third and fourth waves in 1, 2, 4, and 7 suggests that the



Fig. 5. Cyclic voltammograms of 1 and 2 in dry deoxygenated 1,2-dichlorobenzene $(0.1 \text{ M} [(n-Bu)_4 \text{N}][ClO_4])$. Scan rate = 50 mV/s.

Table 4

Half-wave potentials	$(E_{1/2})$	vs. $E^{o_{Fc/Fc}}$) of C ₆₀	, 1,	2,	4,	5, 6,	and 7	Ι.
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Compound	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	$E_{1/2}^{-3/-4}$	Solvent	Ref.
C ₆₀	-1.08	-1.46	-1.90	-2.38	DCB	
1	-1.11	-1.45	-2.02		DCB	а
2	-1.15	-1.48	-2.03		DCB	а
4	-1.06	-1.42	-1.93	-1.95	DCB	[22]
5	-1.13	-1.48	-2.09		DCB	[22]
6	-1.06	-1.42	-1.79		CB	[33]
7	-1.12	-1.46	-1.84		CB	[33]

^a This work.

electron density of C_{60} in species $\mathbf{1}^{3-}$, $\mathbf{2}^{3-}$, $\mathbf{4}^{3-}$, and $\mathbf{7}^{3-}$ is considerably delocalized to the Os metal cluster center [22].

Conclusion

Dppm-substituted fullerene-triosmium cluster derivatives 1 and 2 were successfully prepared by decarbonylation of $Os_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})$ (**3**) with Me₃NO/MeCN in the presence of excess dppm in CB. The dppm ligand bridges two Os centers in compound 1, whereas it chelates a single Os center in compound 2. Electrochemical studies of compounds 1 and 2 revealed that C₆₀mediated electron transfer to the metal cluster takes place in these C_{60} -metal cluster complexes, which have the μ_3 - η^2 : η^2 : η^2 bonding mode

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Appendix A. Supplementary material

CCDC 986771 and 986772 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

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