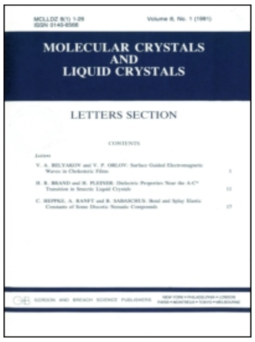
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Synthesis and characterization of triosmium-bis[60]fullerene and bis(metal cluster)[60]fullerene compounds

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ABSTRACT

Triosmium-bis[60]fullerene compound containing dppm ligand, $Os_3(CO)_7(dppm)(C_{60})_2$ (**1**), was synthesized by reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ and dppm ligand with Me_3NO/MeCN. Reaction of $Os_3(CO)_7$(1,2-dppm)$(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ and $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ produced bis(metal-cluster)[60]fullerene compound, $[Os_3(CO)_7(1,2\text{-dppm})](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$ (**2**). Compounds **1** and **2** were characterized by IR, NMR (^1H and ^{31}P), and Mass. Electrochemical property of **1** was confirmed by cyclic voltammetry (CV).

KEYWORDS
fullerene; bis(metal cluster); osmium; rhenium

Introduction

The researchers have been interested in the fullerene compounds due to their potential application in optical, magnetic, electronic, catalytic, and biological fields [1–5]. The metal cluster-C_{60} compounds with $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ bonding mode are remarkably thermal stable and electronic communication between C_{60} and metal centers [4, 5]. Moreover, the reported (metal cluster)-bis[60]fullerene sandwich compounds showed strong electronic communication between the two C_{60} [5, 6]. The electrochemical properties of the compounds can be readily fine-tuned by change of ligands attached to the metal center [4, 5]. C_{60} compounds coordinated to two different metal clusters, $[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$ (*cis*-**1** and *cis*-**2** compounds), were reported with their synthetic methods, characterization, DFT calculation, and electrochemical properties [7]. Recently, I and co-workers reported the preparation and electrochemical properties of $Os_3(CO)_7$(1,2-dppm)$(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ and $Os_3(CO)_7$(1,1-dppm)$(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ [8]. Herein, I report the triosmium-bis[60]fullerene compound containing dppm ligand, $Os_3(CO)_7(dppm)(C_{60})_2$ (**1**), which were prepared through the synthetic method of $Os_3(CO)_7$(1,2-dppm)$(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ and $Os_3(CO)_7$(1,1-dppm)$(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$. Also, I present the bis(metal-cluster)[60]fullerene compound, $[Os_3(CO)_7(1,2\text{-dppm})](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$ (**2**). Compounds **1** and **2** were characterized by spectroscopic methods (IR, ^1H-NMR, and Mass). And, the electrochemical properties of **1** were investigated by cyclic voltammetry (CV).

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Experimental

General comments

Solvents were dried over the appropriate drying agents and distilled immediately before use. Anhydrous trimethylamine *N*-oxide was obtained from $Me_3NO{\cdot}2H_2O$ (98%, Aldrich) by sublimation (three times) at 90-100°C under vacuum. $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ [9] was prepared by the literature methods. Preparative thin layer plates were prepared with silica gel GF_{254} (Type 60, E. Merck).

Preparation of $Os_3(CO)_7(dppm)(C_{60})_2$ (1)

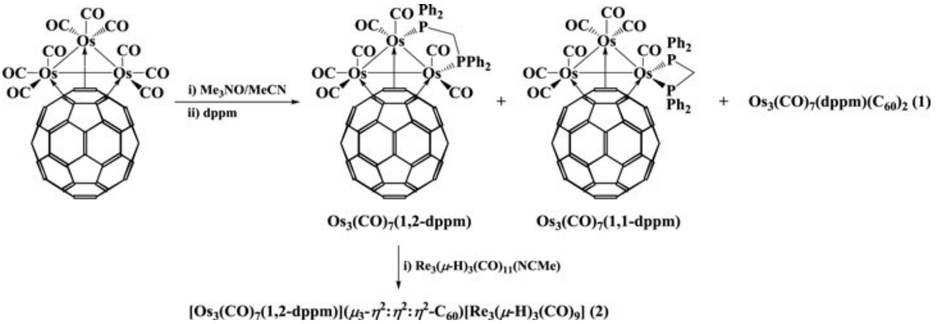
An acetonitrile solution of anhydrous Me_3NO (1.5 mg, 0.0196 mmol) was added dropwise to a chlorobenzene solution (20 mL) of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (30 mg, 0.0194 mmol) at 0°C. The reaction mixture was allowed to warm to room temperature for 30 min. After evaporation of the solvent *in vacuo*, the residue was dissolved in chlorobenzene (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 elution method (three times) on preparative TLC ($CS_2/CH_2Cl_2 = 15{:}1$) produced $Os_3(CO)_7(1,2\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (15 mg, 0.0080 mmol, 41%, $R_f = 0.6$) as a brownish green solid [8], compound $Os_3(CO)_7(1,1\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (12 mg, 0.0064 mmol, 33%, $R_f = 0.5$) as a green solid [8], and compound **1** (5 mg, 0.0019 mmol, 10%, $R_f = 0.4$) as a brown solid. IR(CH_2Cl_2): ν_{CO} 2025 (vs), 1964 (s), 1944 (sh), 1923 (w) cm^{-1}; ^1H NMR (400 MHz, $C_6D_4Cl_2$, 298 K): δ 7.76-7.12 (m, 20H, phenyl), 6.56 (dt, 1H, $J_{HH} = 15.6$ Hz, $J_{PH} = 8.3$ Hz, PCH_2P), 4.43 (dt, 1H, $J_{HH} = 15.6$ Hz, $J_{PH} = 11.5$ Hz, $PC\mathit{H_2}P$); $^{31}P\{^1H\}$ NMR (122 MHz, $C_6D_4Cl_2$, 298 K): δ −34.7 (d, 1P, $J_{PP} = 8.1$ Hz, $\mathit{P}CH_2P$), −51.0 (d, 1P, $J_{PP} = 8.1$ Hz, $PCH_2\mathit{P}$); MS (MALDI-TOF): m/z: 2592.

Preparation of $[Os_3(CO)_7(1,2\text{-dppm})](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$ (2)

$Os_3(CO)_7(1,2\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (10 mg, 0.0053 mmol) and $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ (10 mg, 0.011 mmol) were dissolved in chlorobenzene (20 mL). The solution was refluxed for 2 h. After cooling at room temperature, evaporation of the solvent and purification by multiple elution method on preparative TLC ($CS_2/CH_2Cl_2 = 10{:}1$) produced compound **2** (4 mg, 0.0015 mmol, 28%, $R_f = 0.4$) as a brown solid. IR (CH_2Cl_2) ν_{CO} 2095 (m), 2076 (m), 2050 (m), 2031 (vs), 2007 (vs), 1975 (s) cm^{-1}; ^1H NMR (1,2-$C_6D_4Cl_2$, 298 K) δ 7.84 – 7.20 (m, 20H, $\mathit{Ph_2}PCH_2P\mathit{Ph_2}$), 5.85 (dt, 1H, $J_{HH} = 12.5$ Hz, $J_{PH} = 12.5$ Hz, $PC\mathit{H_2}P$), 4.91 (dt, 1H, $J_{HH} = 12.5$ Hz, $J_{PH} = 12.5$ Hz, $PC\mathit{H_2}P$), −15.31 (s, 1H, $\mu\text{-}H$), −15.50 (s, 1H, $\mu\text{-}H$), −15.65 (s, 1H, $\mu\text{-}H$); $^{31}P\{^1H\}$ NMR (1,2-$C_6D_4Cl_2$, 298 K): δ −18.6 (d, 1P, $J_{PP} = 32.8$ Hz, $\mathit{P}CH_2P$), −22.5 (d, 1P, $J_{PP} = 32.8$ Hz, $PCH_2\mathit{P}$); MALDI TOF : m/z 2685.

Results and discussion

Compound **1** (10%) with $Os_3(CO)_7(1,2\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ [8] and $Os_3(CO)_7(1,1\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ [8] was produced by decarbonylation of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ with $Me_3NO/MeCN$ and then subsequent reaction with dppm in CB at 60°C (Scheme 1).



Scheme 1. Synthesis of **1** and **2**.

Reaction of $Os_3(CO)_7$(1,2-dppm)(μ_3-η^2:η^2:η^2-C_{60}) and $Re_3(\mu\text{-}H)_3(CO)_{11}$(NCMe) in CB at reflux temperature gave bis(metal-cluster)[60]fullerene compound, [$Os_3(CO)_7$(1,2-dppm)](μ_3-η^2:η^2:η^2-C_{60})[$Re_3(\mu\text{-}H)_3(CO)_9$] (**2**) (28%) (Scheme 1). The MALDI TOF mass spectra showed molecular ion isotope multiplets at *m*/*z* 2592 for **1** and 2685 for **2**.

The ^{1}H NMR spectra of **1** and **2** show two doublet of triplet (dt) patterns with an intensity ratio of 1:1 in methylene region due to phosphorous atoms and diastereotopicity of metal combined dppm ligand. For **1**, the spectra displays dt peaks at δ 6.56 ($J_{HH} = 15.6$ Hz, $J_{PH} = 8.3$ Hz) and 4.43 ($J_{HH} = 15.6$ Hz, $J_{PH} = 11.5$ Hz). ^{1}H NMR spectra of **2** shows dt patterns at δ 5.85 ($J_{HH} = 12.5$ Hz, $J_{PH} = 12.5$ Hz) and 4.91 ($J_{HH} = 12.5$ Hz, $J_{PH} = 12.5$ Hz) that is slightly downfield shift than methylene proton peaks of $Os_3(CO)_7$(1,2-dppm)(μ_3-η^2:η^2:η^2-C_{60}) (5.55 ($J_{HH} = 14.3$ Hz, $J_{PH} = 10.7$ Hz) and 4.51 ($J_{HH} = 14.4$ Hz, $J_{PH} = 12.6$ Hz)) [8]. Also, ^{1}H NMR spectra of hydride protons for rhenium cluster part reveal three singlets with 1:1:1 intensity ratio at δ −15.31, −15.50, and −15.65. The ^{31}P{^{1}H} NMR spectra exhibit two doublets at δ −34.7 and −51.0 ($J_{PP} = 8.1$ Hz) for **1**, and −18.6 and −22.5 ($J_{PP} = 32.8$ Hz) for **2** because two phosphine parts of dppm ligand are different environment. ^{31}P NMR spectra for starting compound, $Os_3(CO)_7$(1,2-dppm)(μ_3-η^2:η^2:η^2-C_{60}), of **2** show a singlet at δ −19.4 [8].

Cyclic voltammogram (CV) of **1** is shown to Figure 1. Half-wave potentials ($E_{1/2}$) of free C_{60} [5], $Rh_6(CO)_5(dppm)_2(CNCH_2Ph)$($\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$-$C_{60}$)$_2$ (**3**) [10], $Ir_4(CO)_3(\mu_4\text{-}CH)$-$(PMe_3)_2(\mu\text{-}PMe_2)(CNCH_2Ph)$($\mu$-$\eta^2$:$\eta^2$-$C_{60}$)($\mu_4$-$\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$-$C_{60}$) (**4**) [5], and **1** are provided in Table 1.

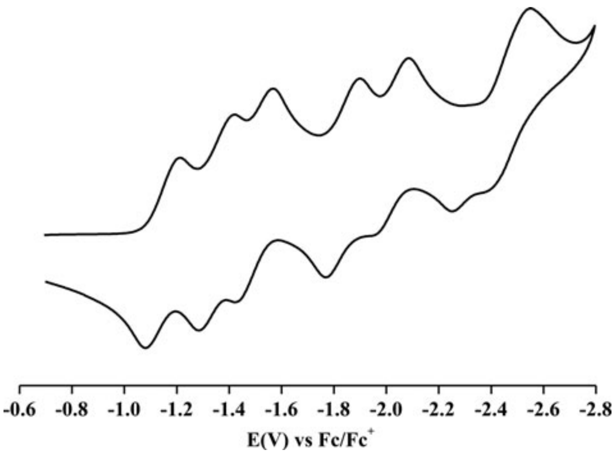


Figure 1. Cyclic voltammograms of **1** in dry deoxygenated 1,2-dichlorobenzene (0.1 M [(n-Bu)$_4$N][ClO$_4$]). Scan rate = 50 mV/s.

Table 1. Half-Wave Potentials ($E_{1/2}$ vs $E^\circ_{Fc/Fc+}$) of Free C_{60}, **3**, **4**, and **1**.

	$E_{1/2}{}^{0/-1}$	$E_{1/2}{}^{-1/-2}$	$E_{1/2}{}^{-2/-3}$	$E_{1/2}{}^{-3/-4}$	$E_{1/2}{}^{-4/-5}$	$E_{1/2}{}^{-5/-6}$	$E_{1/2}{}^{-6/-7}$	solvent
C_{60}	− 1.06	− 1.43	− 1.91	− 2.38				CB
1	− 1.14	− 1.35	− 1.49	− 1.83	− 2.03		− 2.56[a]	CB
3	− 1.19	− 1.38	− 1.62	− 1.86	− 2.12	− 2.41		CB
4	− 1.25	− 1.32	− 1.66	− 1.82	− 2.35	− 2.58		CB

[a] Two-electron process and peak potential of irreversible process.

CV of **1** exhibits five-well separated, reversible, one-electronic redox couples at −1.14, −1.35, −1.49, −1.83, and −2.03 V and one irreversible two-electron redox wave at −2.56 V. The five electron redox waves are sequentially added into the two C_{60} moieties such as C_{60}-Os_3-$C_{60}{}^-$, $C_{60}{}^-$-Os_3-$C_{60}{}^-$, $C_{60}{}^-$-Os_3-$C_{60}{}^{2-}$, $C_{60}{}^{2-}$-Os_3-$C_{60}{}^{2-}$, and $C_{60}{}^{2-}$-Os_3-$C_{60}{}^{3-}$. Similar behaviors were reported bis[60]fullerene compounds, **3** and **4**, and the reversible reduction potentials of **1** show anodic shifts compared to those of **3** and **4**. The irreversible two-electron reduction (−2.56 V) is considered to show due to instability of the compound with high negative charge.

Conclusion

Triosmium-bis[60]fullerene ($Os_3(CO)_7(dppm)(C_{60})_2$, **1**) and bis(metal cluster)[60]fullerene ($[Os_3(CO)_7(1,2\text{-dppm})](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$, **2**) was synthesized and characterized. Electrochemical property of **1** are anodic shift and less stability than those of reported bis[60]fullerenes ($Rh_6(CO)_5(dppm)_2(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})_2$ (**3**) and $Ir_4(CO)_3(\mu_4\text{-}CH)(PMe_3)_2(\mu\text{-}PMe_2)(CNCH_2Ph)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**4**)).

Acknowledgments

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