

Supporting Information

Unusual Coupling Reaction of C₆₀ and Benzonitrile with Triosmium Carbonyls to Generate Fullerodiketimide Cluster Complexes

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Experimental

General Methods. All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Os₃(CO)₁₂ (Strem) and C₆₀ (99%; Bucky USA) were used as received. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded on a Jasco FT/IR-4100 IR spectrometer. ¹H NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 MHz. UV-Vis spectra were recorded from 200 to 700 nm in dichloromethane by using a 1.0 cm quartz cell with an Agilent 8452 spectrophotometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a Bruker Microflex-LT mass spectrometer. High-resolution mass spectra (HRMS) were measured with a Finnigan/Thermo Quest MAT mass spectrometer.

Reaction of Os₃(CO)₁₂ and C₆₀ in Refluxed *o*-Dichlorobenzene Solution. A solution of C₆₀ (80 mg, 0.11 mmol) and Os₃(CO)₁₂ (100 mg, 0.11 mmol), in *o*-dichlorobenzene (50 mL) was refluxed under dinitrogen for 3 h. The volatile materials were removed under vacuum, and the residue was purified by TLC (silica gel), eluting with CS₂. Os₃(CO)₉(μ₃, η⁶-C₆₀) (**1**; 34 mg, 20%) was obtained from the second brown band.

Reaction of Os₃(CO)₁₂ and C₆₀ in Refluxed Benzonitrile/Chlorobenzene Solution. A

solution of C₆₀ (32 mg, 0.044 mmol) and Os₃(CO)₁₂ (20 mg, 0.022 mmol) in benzonitrile (0.5 mL) and chlorobenzene (10 mL) was refluxed under dinitrogen for 10 h. The reaction was monitored by IR and analytical TLC. No evidence for the formation of **1**, **2**, and **3** were observed.

Reaction of Os₃(CO)₁₂ and C₆₀ in Refluxed Chlorobenzene Solution. A solution of C₆₀ (16 mg, 0.022 mmol) and Os₃(CO)₁₂ (10 mg, 0.011 mmol) in chlorobenzene (5 mL) was refluxed under dinitrogen for 24 h. The volatile materials were removed under vacuum, and the residue was purified by TLC (silica gel), eluting with CS₂/CH₂Cl₂ (80:1). Os₃(CO)₉(μ₃,η⁶-C₆₀) (**1**; 4.4 mg, 26%) was obtained.

Reaction of Os₃(CO)₁₀(NCPh)₂ and C₆₀ in Refluxed Chlorobenzene Solution. C₆₀ (14 mg, 0.019 mmol) and Os₃(CO)₁₀(NCPh)₂ (10 mg, 0.0095 mmol) in chlorobenzene (10 mL) was refluxed under dinitrogen for 30 min. The volatile materials were removed under vacuum, and the residue was purified by TLC (silica gel), eluting with CS₂/CH₂Cl₂ (80:1). Compound **1** (18%) was obtained.

Reaction of Os₃(CO)₁₀(NCPh)₂ and C₆₀ in Refluxed Benzonitrile/Chlorobenzene Solution. A solution of C₆₀ (14 mg, 0.019 mmol) and Os₃(CO)₁₀(NCPh)₂ (10 mg, 0.0095 mmol) in benzonitrile (0.5 mL) and *o*-dichlorobenzene (10 mL) was refluxed under dinitrogen for 3 h. The reaction was monitored by IR and analytical TLC. No evidences for the formation of **1**, **2**, and **3** were observed.

Reaction of **1 and C₆₀ in Refluxed Benzonitrile/*o*-Dichlorobenzene Solution.** A solution of C₆₀ (3 mg, 0.004 mmol) and Os₃(CO)₉(μ₃,η⁶-C₆₀) (**1**; 5 mg, 0.0032 mmol) in benzonitrile (0.25 mL) and *o*-dichlorobenzene (5 mL) was refluxed under dinitrogen for 3 h. The reaction was monitored by IR and analytical TLC. No evidence for the formation of **2** and **3** were observed.

Thermolysis of **2 in Refluxed Benzonitrile Solution.** A solution of **2** (5 mg) in benzonitrile (5 mL) was refluxed under dinitrogen for 2 h. The reaction monitored by IR showed slow transformation from **2** to **3**.

Thermolysis of **3 in Refluxed *o*-Dichlorobenzene Solution.** A solution of **3** (5 mg) in benzonitrile *o*-dichlorobenzene (5 mL) was refluxed under dinitrogen for 5 h. The volatile materials were removed under vacuum, and the residue was applied on TLC (silica gel), eluting with

CS₂/CH₂Cl₂ (80:1). This reaction led to severe decomposition of **3**, and only a small amount of **2** (<0.3 mg) was obtained. Formation of **2** is likely from reaction of **3** and CO (from decomposition of **3** in solution).

Cyclic Voltammetric Measurements for 2 and 3. Electrochemical measurements were taken with a CV 50 W system. Cyclic voltammetry was performed with a Pt button working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out with 1 mM solution of **2** and **3**, respectively, in dry *o*-dichlorobenzene containing 0.1 M (*n*-C₄H₉)₄NPF₆ as the supporting electrolyte. Potential was scanned at 10 mV s⁻¹ at 27 °C. Under these conditions, ferrocene shows a reversible one-electron redox wave with E_{1/2} = 420 mV.

Structure Determination for 2 and 3. The crystals of **2**·3CS₂ and **3**·2CS₂ suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The θ range for data collection is 1.24 to 25.11° for **2**·3CS₂ and 1.64 to 25.02° for **3**·3CS₂. Of the 44037 and 63749 reflections collected, 17411 and 16050 reflections were independent for **2**·3CS₂ and **3**·3CS₂, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. Heavily disordered solvent molecules were removed from the diffraction data for **2** (may be 2 CS₂) and **3** (may be 1 CS₂) using the SQUEEZE program. The structures were solved by the direct method and refined by least-square cycles. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.

Table S-1. Crystallographic Data for 2·3CS₂ and 3·2CS₂.

	2·3CS₂	3·2CS₂
chem formula	C ₁₄₉ H ₁₅ N ₃ O ₅ Os ₃ S ₆	C ₁₅₄ H ₂₀ N ₄ O ₄ Os ₃ S ₄
cryst syst	triclinic	monoclinic
fw	2689.60	2688.58
<i>T</i> , K	200(2)	200(2)
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ /c
<i>a</i> , Å	17.2115(11)	27.076(3)
<i>b</i> , Å	18.9698(14)	14.7591(19)
<i>c</i> , Å	19.1654(14)	25.284(3)
<i>α</i> , deg	99.957(5)	90
<i>β</i> , deg	113.190(4)	114.453(7)
<i>γ</i> , deg	111.212(4)	90
<i>V</i> , Å ³	4985.8(6)	9198(2)
<i>Z</i>	2	4
<i>D</i> _{calc} , g cm ⁻³	1.792	1.942
<i>μ</i> , mm ⁻¹	4.009	4.302
<i>R</i> ₁ / <i>wR</i> ₂	0.1050/0.3027	0.0688/0.1594
GOF on <i>F</i> ²	1.017	0.924

Figure S-1. ORTEP diagram of **2** with 30% probability ellipsoids. Selected bond distances (Å): Os1–Os2 = 2.887(1), Os1–Os3 = 2.972(1), Os2···Os3 = 3.282(1), Os1–N1 = 2.06(2), Os2–N1 = 2.03(2), Os2–N2 = 2.00(2), Os3–N2 = 2.04(2), Os1–N3 = 2.13(2), Os3–N3 = 2.04(2), Os3–C15 = 2.08(2), Os2–C28 = 2.26(2), Os2–C29 = 2.33(2), Os2–C87 = 2.27(2), Os2–C88 = 2.27(2), Os3–C89 = 2.19(2), Os3–C90 = 2.25(2), C27–C28 = 1.53(3), C28–C29 = 1.50(3), C29–C30 = 1.54(3), C31–C32 = 1.34(3), C87–C88 = 1.45(2), C88–C89 = 1.47(2), C89–C90 = 1.56(3), N1–C6 = 1.26(2), N2–C13 = 1.27(2), N3–C20 = 1.30(2). Selected bond angles (deg): Os2–Os1–Os3 = 68.14(3), Os1–N1–Os2 = 90.0(6), Os2–N2–Os3 = 108.6(7), Os1–N3–Os3 = 90.9(6), N1–C6–C27 = 115(2), N2–C13–C30 = 112(2), N2–C13–C14 = 116(2), N3–C20–C21 = 127(2).

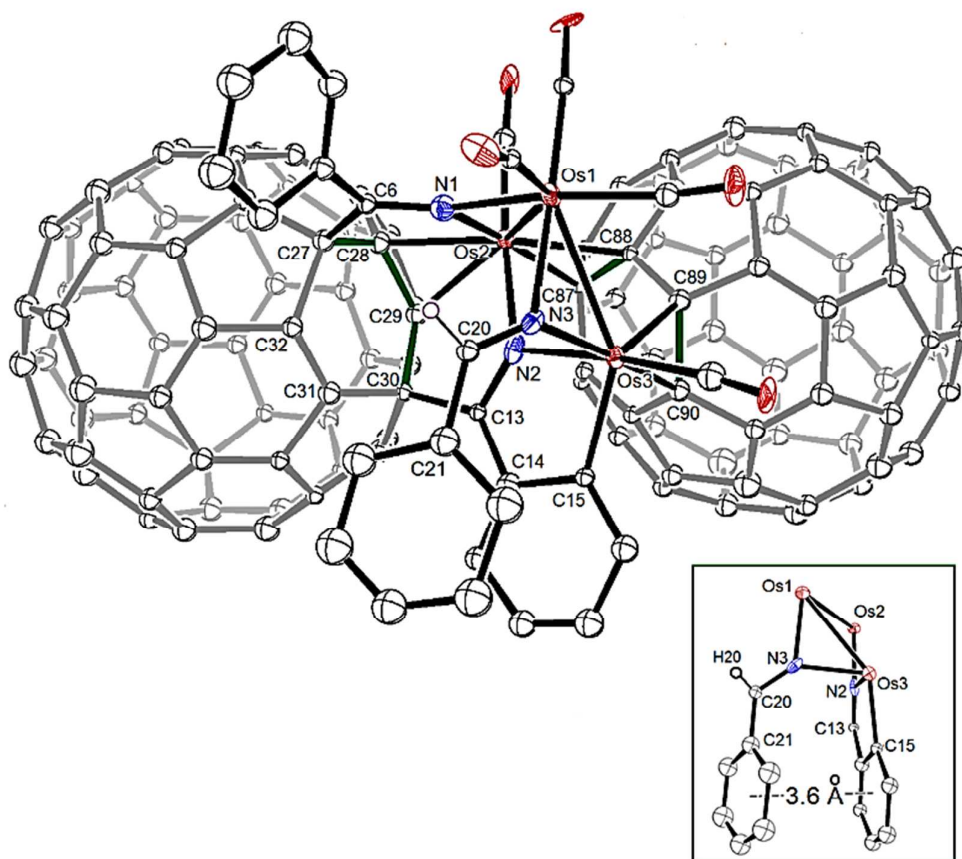


Figure S-2. ORTEP diagram of **3** with 30% probability ellipsoids. Selected bond distances (Å): Os1–Os2 = 2.9437(8), Os1–Os3 = 2.8606(9), Os2···Os3 = 3.331, Os1–N1 = 2.07(1), Os1–N2 = 2.12(1), Os2–N2 = 2.06(1), Os2–N3 = 2.02(1), Os3–N3 = 2.03(1), Os1–N4 = 2.04(1), Os3–N4 = 2.04(1), Os2–C21 = 2.06(1), Os2–C33 = 2.16(1), Os2–C34 = 2.21(1), Os3–C37 = 2.26(1), Os3–C38 = 2.19(1), Os3–C94 = 2.29(1), Os3–C95 = 2.28(1), C33–C34 = 1.49(2), C35–C36 = 1.37(2), C37–C38 = 1.46(2), C93–C94 = 1.57(2), C94–C95 = 1.45(2), C95–C96 = 1.58(2), C97–C98 = 1.38(2), N1–C5 = 1.16(2), N2–C12 = 1.30(2), N3–C19 = 1.25(2), N4–C26 = 1.25(2). Selected bond angles (deg): Os2–Os1–Os3 = 70.02(2), Os1–N1–C5 = 174(1), Os1–N2–Os2 = 89.5(5), Os2–N3–Os3 = 110.6(6), Os1–N4–Os3 = 89.0(4), N1–C5–C6 = 176(2), N2–C12–C13 = 125(1), N3–C19–C20 = 117(1), N3–C19–C93 = 114(1), N4–C26–C27 = 122(1), N4–C26–C96 = 117(1).

