

Syntheses of double- and triple-decker clusters of osmium and cobalt metals linked by cyclotetradeca-1,8-diyne ligands

Tsun-Wei Shiue^a, Wen-Yann Yeh^{a,*}, Gene-Hsiang Lee^b, Shie-Ming Peng^b

^a Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, 70 Lan-Hai Road, Kaohsiung, Taiwan 804

^b Department of Chemistry, National Taiwan University, Taipei, Taiwan 106

Received 26 May 2004; accepted 22 July 2004

Available online 23 August 2004

Abstract

Photoirradiation of $\text{Os}_3(\text{CO})_{10}(\text{C}_{14}\text{H}_{20})$ (**1**) in *n*-hexane produces the double-decker cluster $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})][\text{Os}_3(\text{CO})_{10}]$ (**7**), which can also be prepared from the reaction of $\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})$ (**2**) and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$. Further reaction of **7** with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ affords the triple-decker cluster $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})][\text{Os}_3(\text{CO})_{10}]_2$ (**8**). The bis(diyne) complex $\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2$ (**3**) reacts with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ sequentially to yield the double-decker cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Os}_3(\text{CO})_{10}]$ (**4**) and the triple-decker cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Os}_3(\text{CO})_{10}]_2$ (**5**). Treatment of **3** with $\text{Co}_2(\text{CO})_8$ at room temperature leads to the mixed-metal triple-decker cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Co}_2(\text{CO})_6]_2$ (**6**), while the reaction of **2** and $\text{Co}_2(\text{CO})_8$ produces $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})][\text{Co}_2(\text{CO})_6]_2$ (**9**) and $[\text{Os}_2(\text{CO})_6(\text{C}_{28}\text{H}_{40})][\text{Co}_2(\text{CO})_6]_2$ (**10**). Compound **10**, which involves cluster degradation from Os_3 to Os_2 , has been structurally characterized by an X-ray diffraction study.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Cluster; Osmium; Cobalt; Cyclodiyne

1. Introduction

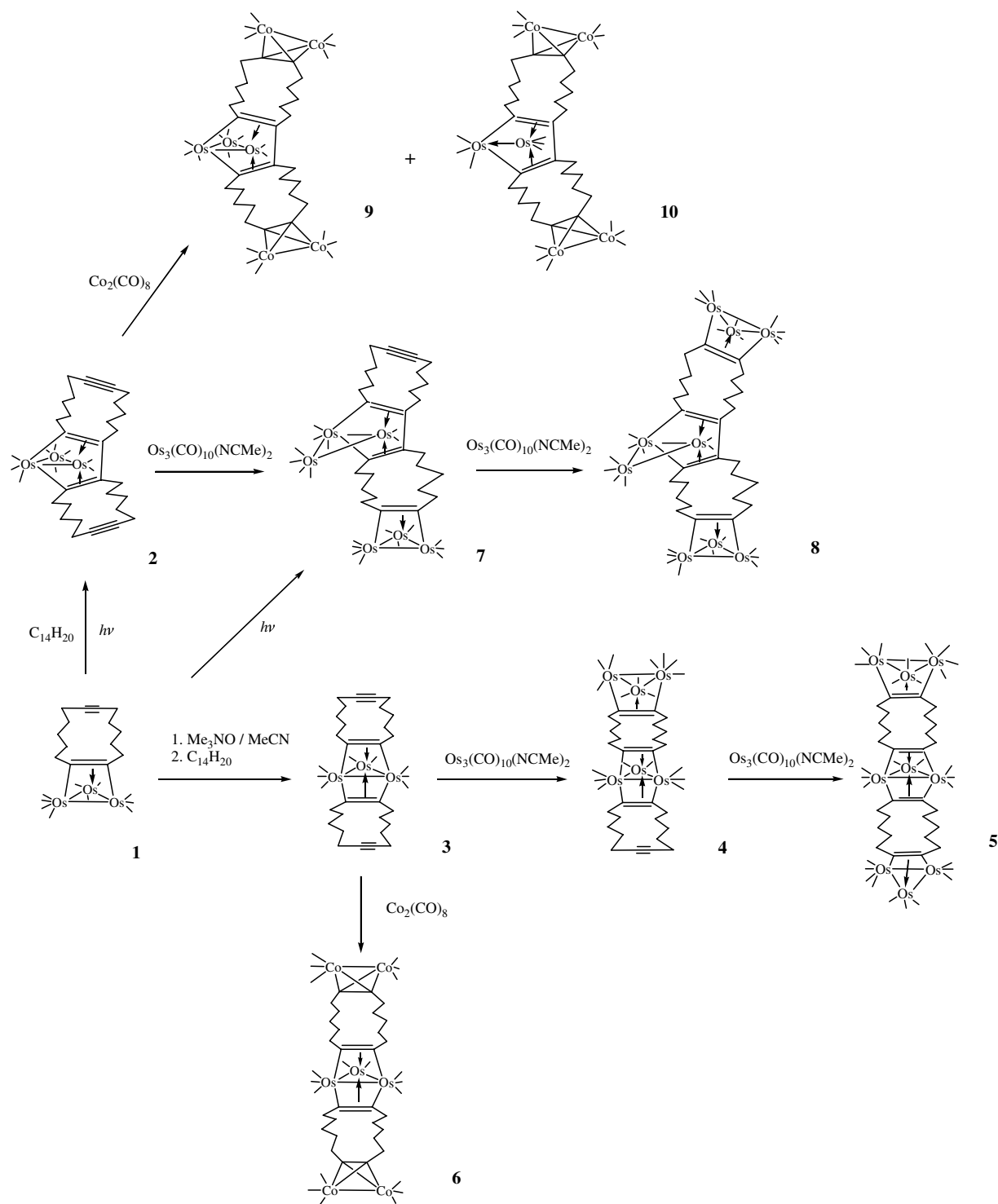
Cyclic dialkynes (or cyclodiyne)s [1] can react with metal carbonyls to give a wide variety of superphanes and cage compounds [2], or serve as bridging units between homo- or heterometallic centers in organometallic compounds [3]. Recently, to construct higher nuclearity clusters with well-defined dimensions provides a new field of chemistry with prospective application in areas including molecular recognition and nanotechnology [4]. We have prepared the triosmium cyclotetradeca-1,8-diyne ($\text{C}_{14}\text{H}_{20}$) complexes $\text{Os}_3(\text{CO})_{10}(\text{C}_{14}\text{H}_{20})$ (**1**), $\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})$ (**2**) and $\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2$ (**3**) [5], and used these complexes as building blocks to assemble a series of beltlike metallacyclodiyne compounds [6]. In this paper we wish to report the syntheses and character-

ization of several double- and triple-decker clusters based on the structures of compounds **1–3**. The reaction pathways are outlined in Scheme 1.

2. Results and discussion

The reaction between cyclotetradeca-1,8-diyne ($\text{C}_{14}\text{H}_{20}$) and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ has been shown to produce **1** and $[\text{Os}_3(\text{CO})_{10}]_2(\text{C}_{14}\text{H}_{20})$ [5]. Since compound **3** can be viewed as an Os_3 -intercalated cyclodiyne, it reacts with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ in hot benzene solvent to afford the double-decker cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Os}_3(\text{CO})_{10}]$ (**4**) and the triple-decker cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Os}_3(\text{CO})_{10}]_2$ (**5**) sequentially. On the other hand, reaction of **3** with two equivalents of $\text{Co}_2(\text{CO})_8$ at ambient temperature affords the mixed-metal cluster $[\text{Os}_3(\text{CO})_8(\text{C}_{14}\text{H}_{20})_2][\text{Co}_2(\text{CO})_6]_2$ (**6**) in good isolated yield.

* Corresponding author. Tel.: 886752520003927; fax: 88675253908.
E-mail address: wenyann@mail.nsysu.edu.tw (W.-Y. Yeh).



Scheme 1.

Previously, the osmacyclopentadienyl complex **2** was obtained from photoirradiation of **1** in the presence of $\text{C}_{14}\text{H}_{20}$ ligand [5]. Since compound **1** contains a pendant alkyne moiety and an open Os_3 face, irradiation of **1** itself results in an intermolecular alkyne-insertion to generate the double-decker cluster $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})]$

$[\text{Os}_3(\text{CO})_{10}]$ (**7**). This reaction, however, was carried out for a short period (1 h) to recover **1** in 81%, while extending the irradiation time did not improve the yield of **7** but leading to a complex mixture, which is likely due to continuous photoreactions of the products. An alternative method to make **7** is by treating **2** with

$\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ at 60 °C for 20 min. Further reaction of **7** and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ affords the triple-decker cluster $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})][\text{Os}_3(\text{CO})_{10}]_2$ (**8**), where the two ending alkyne groups of **2** are each coordinated to an $\text{Os}_3(\text{CO})_{10}$ species. On the other hand, compound **2** reacts with a slight excess of $\text{Co}_2(\text{CO})_8$ at ambient temperature to produce the mixed-metal triple-decker clusters $[\text{Os}_3(\text{CO})_9(\text{C}_{28}\text{H}_{40})][\text{Co}_2(\text{CO})_6]_2$ (**9**) and $[\text{Os}_2(\text{CO})_6(\text{C}_{28}\text{H}_{40})][\text{Co}_2(\text{CO})_6]_2$ (**10**), with the formation of **10** involving nuclear degradation from a triosmium into a diosmium linkage.

The new compounds **4–10** form stable, colored solids, where **4** and **5** are yellow, **7** and **8** are green, and **6**, **9** and **10** are brown. Their solubility in organic solvents decreases as the ending alkyne moieties are coordinated to the $\text{Os}_3(\text{CO})_{10}$ cluster, such that **2** and **3** are soluble in *n*-hexane, **4** and **7** are soluble in benzene and dichloromethane but slightly soluble in *n*-hexane, while **5** and **8** show a poor solubility in dichloromethane and THF. On the contrary, the dicobalt-capped clusters **6**, **9** and **10** are plenty soluble in common organic solvents. The IR spectra in the carbonyl region for **4** and **5** are apparently the combination of the spectra of **3** and **1**, and for **7** and **8** are the combination of **2** and **1**.

Compound **4** exhibits the expected C_s symmetry in solution. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays four signals for the carbonyl carbons of $\text{Os}_3(\text{CO})_8$ moiety, one broad signal for the fluxional carbonyl carbons of $\text{Os}_3(\text{CO})_{10}$ moiety [7], three signals at 168.2, 166.9 and 148.3 ppm for the coordinated alkyne carbons, one signal at 80.5 ppm for the pendant alkyne carbons, and ten signals in the range 52.7–18.1 ppm for the methylene

carbons. In contrast, the bending configuration of **7** gives no symmetry, such that its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presents 28 carbon resonances for the $\text{C}_{28}\text{H}_{40}$ ligand. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** depicts one carbonyl signal for the $\text{Co}_2(\text{CO})_6$ group, three carbonyl signals for the $\text{Os}_3(\text{CO})_8$ group, two signals at 165.9 and 98.1 ppm for the alkyne carbons bonded to the Os and Co atoms, respectively, and five signals in the range 51.4–27.9 ppm for the methylene carbons, consistent with a C_{2v} symmetry for the proposed structure (Scheme 1). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **9** and **10** are compatible in the organic ligand region to show two signals for the osmacyclopentadienyl carbons, two signals for the alkyne carbons bonded to the Co atoms, and ten signals for the methylene carbons, in agreement with the proposed structures with a time-averaged C_s symmetry in solution. Although the ^{13}C NMR and FAB mass spectra for **5** and **8** are not obtainable due to a poor solubility in organic solvents, their constitution and configuration can be assigned on the basis of elemental analyses and the IR spectra in comparison with compounds **2**, **4**, **7** and $[\text{Os}_3(\text{CO})_{10}]_2(\text{C}_{28}\text{H}_{40})$ [5].

Compound **10** forms dark-red crystals. The ORTEP diagram of **10** is shown in Fig. 1, and the selected bond distances and bond angles are collected in Table 1. The molecule consists of a $\text{C}_4(\text{C}_{12}\text{H}_{20})_2$ link, which is connected with a $\text{Os}_2(\text{CO})_6$ group in the middle and two $\text{Co}_2(\text{CO})_6$ groups at the ending sites. The osmium and cobalt atoms are each associated with three terminal carbonyl ligands, with the M–C–O angles in the range 174(2)–179(1)°. The Os(1) atom and the diene C(19)–C(22) atoms are coplanar to within ± 0.02 Å, yielding

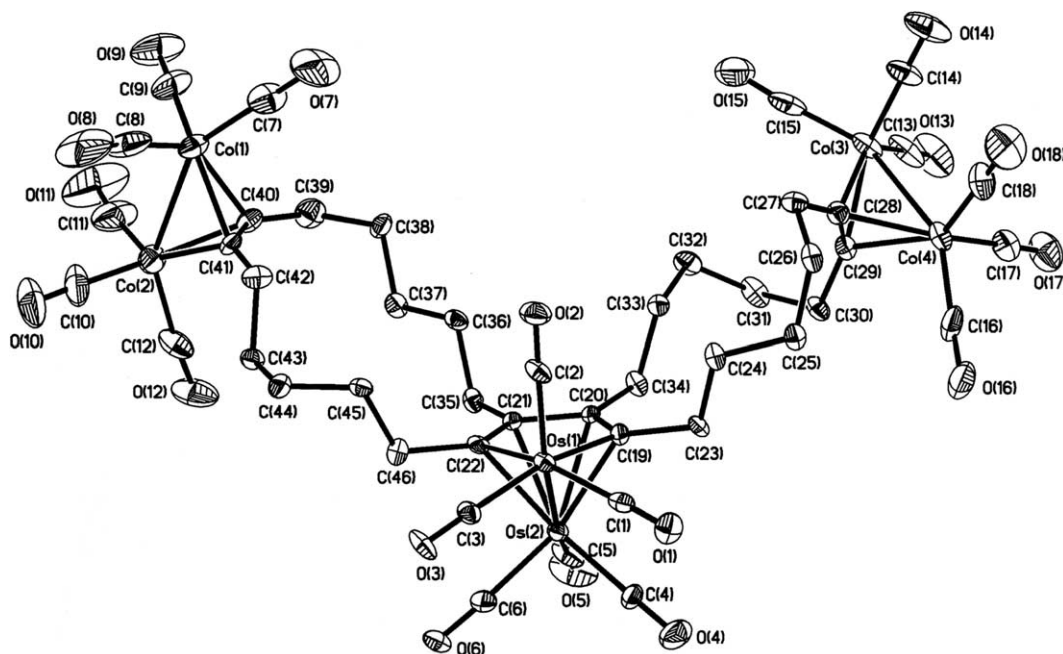


Fig. 1. ORTEP drawing of **10**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond distances (Å) and bond angles (°) for **10**

Bond distances			
Os(1)–Os(2)	2.7551(5)	Os(1)–C(19)	2.095(9)
Os(1)–C(22)	2.090(9)	Os(2)–C(19)	2.322(8)
Os(2)–C(20)	2.265(9)	Os(2)–C(21)	2.255(9)
Os(2)–C(22)	2.314(9)	C(19)–C(20)	1.401(13)
C(20)–C(21)	1.466(12)	C(21)–C(22)	1.429(13)
Co(1)–Co(2)	2.461(2)	Co(3)–Co(4)	2.463(2)
Co(1)–C(40)	1.966(10)	Co(1)–C(41)	1.968(10)
Co(2)–C(40)	1.958(11)	Co(2)–C(41)	1.969(10)
Co(3)–C(28)	1.990(10)	Co(3)–C(29)	1.968(9)
Co(4)–C(28)	1.983(10)	Co(4)–C(29)	1.970(9)
C(28)–C(29)	1.303(13)	C(40)–C(41)	1.314(14)
Bond angles			
C(19)–Os(1)–C(22)	77.8(4)	C(20)–C(19)–Os(1)	116.3(7)
C(19)–C(20)–C(21)	115.9(8)	C(22)–C(21)–C(20)	112.6(8)
C(21)–C(22)–Os(1)	117.3(6)	C(19)–Os(1)–Os(2)	55.2(2)
C(19)–Os(2)–Os(1)	47.8(2)	Os(1)–C(19)–Os(2)	77.0(3)
C(22)–Os(1)–Os(2)	55.0(2)	C(22)–Os(2)–Os(1)	47.7(2)
Os(1)–C(22)–Os(2)	77.3(3)	C(21)–Os(2)–C(22)	36.4(3)
C(22)–C(21)–Os(2)	74.0(5)	C(21)–C(22)–Os(2)	69.6(5)
C(21)–Os(2)–C(20)	37.8(3)	C(21)–C(20)–Os(2)	70.7(5)
C(20)–C(21)–Os(2)	71.4(5)	C(20)–Os(2)–C(19)	35.5(3)
C(20)–C(19)–Os(2)	70.0(5)	C(19)–C(20)–Os(2)	74.4(5)

an osmacyclopentadienyl framework [8]. Thus, the coordination about the Os(1) atom can be described as a distorted octahedron, and the Os(2) atom as a three-legged piano stool by considering the metallacycle as an η^5 ligand. The Os(1)–Os(2) length is 2.7551(5) Å, typical of an osmium–osmium single bond, while the C(19–22)–Os(2) distances show substantial variation, ranging from 2.255(9) to 2.322(8) Å. The alkyne C(28)–C(29) and C(40)–C(41) units apparently donate four π -electrons to each dicobalt system in a \perp -bonding mode to give a

quasi-tetrahedral core with the averaged C–Co distances of 1.97 Å. The Co(1)–Co(2) and Co(3)–Co(4) lengths are equal, being 2.46 Å.

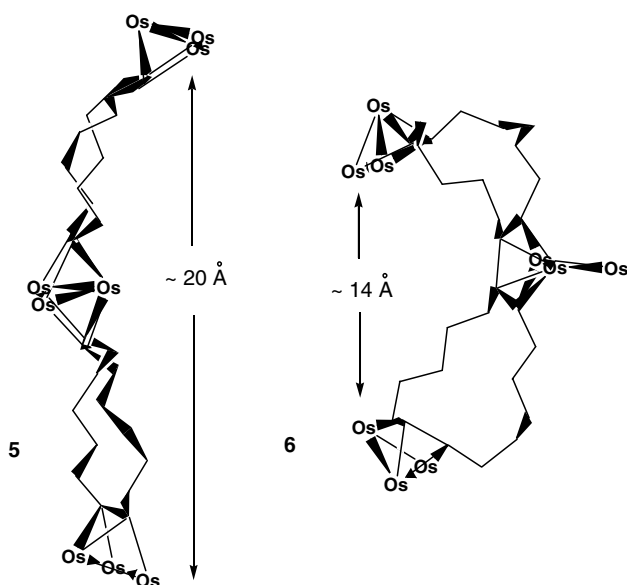
In summary, compounds **2** and **3** can react with Os₃(CO)₁₀(NCMe)₂ and Co₂(CO)₈ to give the double- and triple-decker clusters **4–10**, which are of interest within the context of supramolecular chemistry [9]. The lengths of these triple cluster compounds are 1–2 nm, such that the two Co₂ units in **10** are separated by 13 Å, and the distances between the two ending Os₃ groups are estimated to be 20 and 14 Å for **5** and **6**, respectively (Scheme 2). It is promising that further treatment of **5** with Me₃NO/MeCN or photoirradiation of **8** in the presence of C₁₄H₂₀ ligand can lead to higher nuclearity cluster oligomers with a straight or curled metallacyclic chain. The investigation is in progress in our laboratory.

3. Experimental

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques [10]. Cyclotetradeca-1,8-diene (C₁₄H₂₀) [11], Os₃(CO)₁₀(NCMe)₂ [12], Os₃(CO)₁₀(C₁₄H₂₀) (**1**) [5], Os₃(CO)₉(C₂₈H₄₀) (**2**) [5], and Os₃(CO)₈(C₁₄H₂₀)₂ (**3**) [6] were prepared by literature methods. Co₂(CO)₈ (from Strem) was used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded with a 0.1 mm path-length CaF₂ solution cell on a Hitachi I-2001 IR spectrometer. ¹H and ¹³C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 125.7 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded on a VG Blotch-5022 or a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

3.1. Photoirradiation of **1** to give **7**

This reaction was carried out in an ACE microscale photoreaction vessel equipped with an immersed Pen-Ray 5.5 W low-pressure, cold cathode, mercury gaseous discharge lamp. Os₃(CO)₁₀(C₁₄H₂₀) (**1**; 100 mg, 0.096 mmol) was dissolved in *n*-hexane (15 ml) and the solution was irradiated for 1 h with dinitrogen slowly bubbling through the solution. During the reaction, the solution color changed gradually from orange to gray-yellow. The solvent was removed on a rotary evaporator, and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane as eluent (1:4, v/v). The unreacted compound **1** (81 mg) was recovered from the first yellow band. The major green band yielded [Os₃(CO)₉-



Scheme 2.

(C₂₈H₄₀)[Os₃(CO)₁₀] (**7**; 11 mg, 59% based on **1** consumed). Anal. Calc. for C₄₇H₄₀O₁₉Os₆: C, 27.51; H, 1.95. Found: C, 27.55; H, 2.40%. MS (FAB): *m/z* 2048 (M⁺, ¹⁹⁰Os). IR (CH₂Cl₂, ν_{CO}): 2100m, 2060s, 2040vs, 2012s, 1994vs, 1964s, 1918w cm⁻¹. ¹H NMR (CDCl₃, 23 °C): 3.30–1.27 (m, CH₂) ppm. ¹³C{¹H} NMR (C₆D₆, 23 °C): 178.2, 176.0, 175.9 (Os₃(CO)₉), 177.2 (br, Os₃(CO)₁₀), 173.7, 165.3, 128.5, 126.3 (μ-C₄Os), 148.8, 148.4 (C≡C–Os₃(CO)₁₀), 82.5, 80.1 (free C≡C), 53.7, 51.5, 50.2, 45.1, 43.9, 36.9, 34.3, 33.8, 32.6, 32.0, 31.7, 31.3, 29.6, 28.9, 28.5, 28.2, 27.8, 26.6, 19.4, 17.6 (CH₂) ppm.

3.2. Preparation of **7** from **2** and Os₃(CO)₁₀(NCMe)₂

Os₃(CO)₉(C₂₈H₄₀) (**2**; 20 mg, 0.017 mmol) and Os₃(CO)₁₀(NCMe)₂ (11 mg, 0.012 mmol) were dissolved in benzene (10 ml) and the solution was heated at 60 °C for 20 min. After cooling the solution to ambient temperature, the solvent was removed on a rotary evaporator and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane (1:4, v/v) as eluent. The starting compound **2** (10 mg) was recovered from the first blue band. The second green band afforded compound **7** (12 mg, 70% based on **2** consumed).

3.3. Preparation of **8** from **2** and Os₃(CO)₁₀(NCMe)₂

Os₃(CO)₉(C₂₈H₄₀) (**2**; 15 mg, 0.012 mmol) and Os₃(CO)₁₀(NCMe)₂ (45 mg, 0.048 mmol) were dissolved in benzene (20 ml). The solution was heated at 60 °C for 20 min, yielding a green precipitate. The precipitate was collected by filtration and washed with benzene to give [Os₃(CO)₉(C₂₈H₄₀)]Os₃(CO)₁₀ (**8**; 24 mg, 69%). Anal. Calc. For C₅₇H₄₀O₂₉Os₉: C, 23.60; H, 1.38. Found: C, 23.92; H, 1.47%. IR (CH₂Cl₂, ν_{CO}): 2100m, 2060s, 2040vs, 2012s, 1994vs, 1964s, 1918w cm⁻¹.

3.4. Preparation of **8** from **7** and Os₃(CO)₁₀(NCMe)₂

Compound **7** (5 mg, 0.0024 mmol) and Os₃(CO)₁₀(NCMe)₂ (5 mg, 0.005 mmol) were dissolved in benzene (3 ml). The solution was heated at 60 °C for 20 min, yielding a green precipitate of **8** (5 mg, 72%).

3.5. Preparation of **4** from **3** and Os₃(CO)₁₀(NCMe)₂

Os₃(CO)₈(C₁₄H₂₀)₂ (**3**; 40 mg, 0.034 mmol) and Os₃(CO)₁₀(NCMe)₂ (22 mg, 0.024 mmol) were dissolved in benzene (20 ml) and the solution was heated at 60 °C for 20 min. The solvent was removed on a rotary evaporator and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane (1:4, v/v) as eluent. The unreacted compound **3** (19 mg) was recovered from the first yellow band. The second yellow band afforded [Os₃(CO)₈(C₁₄H₂₀)₂][Os₃(CO)₁₀] (**4**; 25 mg, 69% based on **3**

consumed). Anal. Calc. for C₄₆H₄₀O₁₈Os₆: C, 27.32; H, 1.99. Found: C, 27.75; H, 2.07%. MS (FAB): *m/z* 2020 (M⁺, ¹⁹⁰Os). IR (CH₂Cl₂, ν_{CO}): 2100w, 2080m, 2060s, 2040vs, 2012vs, 2000vs, 1972m, 1936w cm⁻¹. ¹H NMR (CDCl₃, 23 °C): 3.83 (m, 2H), 3.59 (m, 2H), 3.47 (m, 2H), 3.20 (m, 2H), 3.08 (m, 2H), 2.30 (m, 6H), 2.13 (m, 6H), 1.76–1.51 (m, 18H) ppm. ¹³C{¹H} NMR (CDCl₃, 23 °C): 181.0, 178.7, 178.5, 165.8 (Os₃(CO)₈), 176.9 (br, Os₃(CO)₁₀), 168.2, 166.9 (C≡C–Os₃(CO)₈), 148.3 (C≡C–Os₃(CO)₁₀), 80.5 (free C≡C), 52.7, 50.9, 49.4, 34.3, 33.9, 33.0, 28.6, 27.9, 26.5, 18.1 (CH₂) ppm.

3.6. Preparation of **5** from **3** and Os₃(CO)₁₀(NCMe)₂

Os₃(CO)₈(C₁₄H₂₀)₂ (**3**; 19 mg, 0.016 mmol) and Os₃(CO)₁₀(NCMe)₂ (60 mg, 0.064 mmol) were dissolved in benzene (25 ml). The solution was heated at 60 °C for 20 min, yielding a yellow precipitate. The precipitate was collected by filtration, and washed with benzene to give [Os₃(CO)₈(C₁₄H₂₀)₂][Os₃(CO)₁₀]₂ (**5**; 40 mg, 87%). Anal. Calc. for C₅₆H₄₀O₂₈Os₉: C, 23.41; H, 1.40. Found: C, 23.74; H, 1.65%. IR (CH₂Cl₂, ν_{CO}): 2100w, 2080m, 2060s, 2040vs, 2012vs, 2000vs, 1972m, 1936w cm⁻¹.

3.7. Preparation of **5** from **4** and Os₃(CO)₁₀(NCMe)₂

Compound **4** (5 mg, 0.0025 mmol) and Os₃(CO)₁₀(NCMe)₂ (5 mg, 0.005 mmol) were dissolved in benzene (3 ml). The solution was heated at 60 °C for 20 min to yield a yellow precipitate, characterized as **5** (6 mg, 84%).

3.8. Preparation of **6**

Os₃(CO)₈(C₁₄H₂₀)₂ (**3**; 25 mg, 0.021 mmol) and Co₂(CO)₈ (18 mg, 0.053 mmol) were dissolved in *n*-hexane (35 ml) and the solution was stirred at ambient temperature for 1 h. The solvent was evaporated and the residue was subjected to TLC, with *n*-hexane as eluent. The major brown band afforded [Os₃(CO)₈(C₁₄H₂₀)₂][Co₂(CO)₆]₂ (**6**; 30 mg, 82%). Anal. Calc. for C₄₈H₄₀O₂₀Co₄Os₃: C, 33.06; H, 2.31. Found: C, 33.27; H, 2.60%. IR (CH₂Cl₂, ν_{CO}): 2084m, 2044vs, 2012vs, 2000vs, 1970m, 1936w cm⁻¹. ¹H NMR (CDCl₃, 23 °C): 3.64 (m, 4H), 3.58 (m, 4H), 3.04 (m, 8H), 1.90 (m, 8H), 1.80 (m, 8H), 1.68 (m, 4H), 1.63 (m, 4H) ppm. ¹³C{¹H} NMR (CDCl₃, 23 °C): 200.3 (OC–Co), 181.0, 178.6, 165.8 (OC–Os), 165.9 (C≡C–Os₃), 98.1 (C≡C–Co₂), 51.4, 34.2, 31.6, 30.7, 27.9 (CH₂) ppm.

3.9. Reaction of **2** and Co₂(CO)₈

Os₃(CO)₉(C₂₈H₄₀) (**2**; 30 mg, 0.025 mmol) and Co₂(CO)₈ (22 mg, 0.064 mmol) were dissolved in *n*-hexane (35 ml) and the solution was stirred at ambient

temperature for 1 h. The solvent was evaporated and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane (1:4, v/v) as eluent. Isolation of the first and second brown bands afforded [Os₃(CO)₉(C₂₈H₄₀)] [Co₂(CO)₆]₂ (**9**; 18 mg, 41%) and [Os₂(CO)₆(C₂₈H₄₀)] [Co₂(CO)₆]₂ (**10**; 10 mg, 27%), respectively.

3.9.1. [Os₃(CO)₉(C₂₈H₄₀)] [Co₂(CO)₆]₂ (**9**)

IR (CH₂Cl₂, ν_{CO}): 2104w, 2084m, 2040s, 1998vs, 1966m, 1914w cm⁻¹. ¹H NMR (CD₂Cl₂, 23 °C): 3.22–1.27 (m, CH₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 23 °C): 201.1 (CO–Co), 177.7, 176.0, 175.9 (CO–Os), 168.0, 129.9 (μ–C₄Os), 99.1, 98.9 (C≡C–Co₂), 44.0, 34.4, 33.9, 33.3, 32.5, 31.3, 30.9, 30.8, 29.2, 28.8 (CH₂) ppm.

3.9.2. [Os₂(CO)₆(C₂₈H₄₀)] [Co₂(CO)₆]₂ (**10**)

IR (CH₂Cl₂, ν_{CO}): 2080m, 2040s, 1998vs, 1960m cm⁻¹. ¹H NMR (CD₂Cl₂, 23 °C): 3.13–1.27 (m, CH₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 23 °C): 200.1 (CO–Co), 184.1, 179.0, 176.0 (CO–Os), 155.7, 123.5 (μ–C₄Os), 98.9, 98.7 (C≡C–Co₂), 42.7, 34.8, 34.6, 33.8, 33.6, 31.4, 30.9, 29.6, 29.1, 29.0 (CH₂) ppm.

3.10. Structure determination for **10**

The Crystal of **10** suitable for an X-ray diffraction study was mounted in a thin-walled glass capillary and aligned on the Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data was collected at 150 K. All data were corrected for the effects of absorption. The structure was solved by the direct method and refined by full-matrix least-square on F². The program used was the SHELXTL package [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included but not re-

fined. A summary of relevant crystallographic data is provided in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis of **10** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 231492. Copy of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgement

We are grateful for support of this work by the National Science Council of Taiwan.

References

- [1] (a) M. Nakagawa Topics in Nonbenzenoid Aromatic Chemistry, vol. 1, Hirokawa Publishing Co., Tokyo, 1973; (b) F. Sondheimer, Acc. Chem. Res. 5 (1972) 81; (c) R. Gleiter, W. Schäfer, Acc. Chem. Res. 23 (1990) 369; (d) W.J. Youngs, C.A. Tessier, J.D. Bradshaw, Chem. Rev. 99 (1999) 3153.
- [2] (a) F. Vögtle, Cyclophane Chemistry: Synthesis, Structures and Reactivity, Wiley, Chichester, UK, 1993; (b) D.J. Cram, J.M. Cram, Container Molecules and Their Guests, The Royal Society of Chemistry, London, 1994; (c) R. Gleiter, M. Merger, Angew. Chem. Int. Ed. Engl. 36 (1997) 2426; (d) R.B. King, A. Efraty, J. Am. Chem. Soc. 94 (1972) 3021; (e) R.B. King, M.N. Ackermann, J. Organomet. Chem. 67 (1974) 431; (f) C.M. Adams, E.M. Holt, Organometallics 9 (1990) 980.
- [3] (a) B.J. Rausch, R. Gleiter, F. Rominger, J. Chem. Soc. Dalton Trans. (2002) 2219; (b) M.-A. Hsu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, J. Organomet. Chem. 588 (1999) 32; (c) M.-A. Hsu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Inorg. Chim. Acta 294 (1999) 232.
- [4] (a) K.E. Drexler, Molecular Machinery, Manufacturing and Computation, Wiley, New York, 1992; (b) S. Onaka, M. Otsuka, Chem. Lett. (1995) 269; (c) D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH, New York, 1990; (d) A.J. Amoroso, B.F.G. Johnson, J. Lewis, A.D. Massey, P.R. Raithby, W.T. Wong, J. Organomet. Chem. 440 (1992) 219; (e) P. Braunstein, L.A. Oro, P.R. Raithby, Metal Clusters in Chemistry, Wiley-VCH, Weinheim, Germany, 1999; (f) W.-Y. Yeh, C.-Y. Wu, L.-W. Chiou, Organometallics 18 (1999) 3547; (g) N.T. Lucas, E.G.A. Notaras, S. Petrie, R. Stranger, M.G. Humphrey, Organometallics 22 (2003) 708; (h) M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46; (i) S. Leininger, B. Oelenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.
- [5] W.-Y. Yeh, M.-A. Hsu, S.-M. Peng, G.-H. Lee, Organometallics 18 (1999) 880.

Table 2
Crystal data and refinement details for **10**

Formula	C ₄₆ H ₄₀ Co ₄ O ₁₈ Os ₂
<i>T</i> (K)	150(1)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	8.8537(5)
<i>b</i> (Å)	14.8788(8)
<i>c</i> (Å)	39.035(2)
β (°)	94.382(2)
<i>V</i> (Å ³)	5127.2(5)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.939
<i>F</i> (000)	2880
μ (mm ⁻¹)	6.271
θ range (°)	1.05–27.50
<i>R</i> ₁	0.0569
<i>wR</i> ₂	0.1020
GOF on <i>F</i> ²	1.004

- [6] W.-Y. Yeh, T.-W. Shiue, S.-M. Peng, G.-H. Lee, *Organometallics* 22 (2003) 2990.
- [7] E. Rosenberg, J. Bracker-Novak, R.W. Gellert, S. Aime, R. Gobetto, D. Osella, *J. Organomet. Chem.* 365 (1989) 163.
- [8] (a) W.-Y. Yeh, S.C.N. Hsu, S.-M. Peng, G.-H. Lee, *Organometallics* 17 (1998) 2477;
(b) P.J. Harris, J.A.K. Howard, S.A.R. Knox, R.P. Phillips, F.G.A. Stone, P. Woodward, *J. Chem. Soc. Dalton Trans.* (1976) 377;
(c) R.P. Dodge, O.S. Mills, V. Schomaker, *Proc. Chem. Soc. London* (1963) 380.
- [9] J.W. Steed, J.L. Atwood, *Supramolecular Chemistry*, Wiley, New York, 2000.
- [10] D.F. Shriver, M.A. Drezdson, *The Manipulation of Air-Sensitive Compounds*, second ed., Wiley, New York, 1986.
- [11] R. Gleiter, R. Merger, B. Treptow, W. Wittwer, G. Pflasterer, *Synthesis* (1993) 558.
- [12] D. Braga, F. Grepioni, E. Parisini, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, J. Lewis, M. Martinelli, *J. Chem. Soc. Dalton Trans.* (1993) 1891.
- [13] G.M. Sheldrick, *SHELXTL-97*, University of Göttingen, Germany, 1997.