Syntheses of Beltlike Polycyclodiyne Intercalated with Triosmium Carbonyl Clusters

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Received March 10, 2003

The bis(cyclodiyne) complex $\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_{20})_2$ (**4**) has been prepared by treating $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_{20})$ (**1**) with Me_3NO in the presence of cyclotetradeca-1,8-diyne ($\text{C}_{14}\text{H}_{20}$) ligand. Thermolysis of **4** leads to the osmacyclopentadiene complex $\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^4\text{-C}_{14}\text{H}_{20})_2$ (**3**). The tris(cyclodiyne) complex $(\text{Os}_3(\text{CO})_8)_2(\mu_3, \mu_3\text{-}\eta^2, \eta^2\text{-C}_{14}\text{H}_{20})(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_{20})_2$ (**5**) is obtained from the reaction of $(\text{Os}_3(\text{CO})_{10})_2(\mu_3, \mu_3\text{-}\eta^2, \eta^2\text{-C}_{14}\text{H}_{20})$ (**2**) with Me_3NO and $\text{C}_{14}\text{H}_{20}$, while photoirradiation of **2** and $\text{C}_{14}\text{H}_{20}$ affords the bis(osmacyclopentadiene) complex $(\text{Os}_3(\text{CO})_9)_2(\mu, \mu\text{-}\eta, \eta^4\text{-C}_{14}\text{H}_{20})_3$ (**6**). Co-irradiation of **3** and **1** also produces **6**. Compounds **3**, **4**, **5**, and **6** can be viewed as cluster-intercalated, beltlike polycyclodiyne. The structures of **4** and **6** (two isomers) have been determined by an X-ray diffraction study.

Introduction

Cyclic dialkynes (or cyclodiyne)s¹ are versatile starting materials for the synthesis of superphanes and cage compounds.² In addition, interest has been stimulated by the potential for these molecules to serve as bridging units between homo- or heterometallic centers in organometallic compounds.³ Recently, constructing 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 $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_{20})$ (**1**), $(\text{Os}_3(\text{CO})_{10})_2(\mu_3, \mu_3\text{-}\eta^2, \eta^2\text{-C}_{14}\text{H}_{20})$ (**2**), and $\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^4\text{-C}_{14}\text{H}_{20})_2$ (**3**).⁵ Since compounds **1–3** contain

pendant alkyne ligands and/or open Os_3 faces, it is promising to construct multiple cluster systems by using these complexes as building blocks. Now we report the syntheses of the unprecedented Os_3 -intercalated polycyclodiyne **4–6**. The reaction pathways are outlined in Scheme 1.

Results and Discussion

To a mixture of **1** and $\text{C}_{14}\text{H}_{20}$ in dichloromethane was added 2 equiv of Me_3NO (to remove CO) in MeCN at room temperature to generate the bis(cyclodiyne) complex $\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_{20})_2$ (**4**) in 32% yield after purification by TLC and crystallization.⁶ Compound **4** forms an air-stable yellow crystalline solid. Thermolysis of **4** results in coupling of the coordinated alkynes to yield **3**, while heating **1** produces the hydrido allene complex $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-C}_{14}\text{H}_{19})$.⁵ The ORTEP diagram of **4** is shown in Figure 1. The metal parts are based upon a triangular array of osmium atoms in which the $\text{Os}(1)\text{--Os}(2)$ distance is significantly longer than the other two intermetallic distances. The $\text{Os}(1)$ and $\text{Os}(2)$ atoms are each associated with three terminal carbonyl ligands, while the $\text{Os}(3)$ atom is linked with two. The alkyne $\text{C}(9)\text{--C}(10)$ and $\text{C}(23)\text{--C}(24)$ units are asymmetrically bonded to the osmium atoms, formally forming π bonds to the $\text{Os}(3)$ atom and σ bonds to the $\text{Os}(1)$ and $\text{Os}(2)$ atoms. The atoms $\text{C}(9)$, $\text{C}(10)$, $\text{Os}(1)$, and $\text{Os}(2)$ and the atoms $\text{C}(23)$, $\text{C}(24)$, $\text{Os}(1)$, and $\text{Os}(2)$ are coplanar to within 0.1 Å, and the dihedral angle between the two planes is 108°. Thus, the $[\text{C}_4\text{Os}_2]$ fragment may also be described as a diosma-Dewar-

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(6) The analogous bis(alkyne) complexes $\text{Os}_3(\text{CO})_8(\text{C}_2\text{Ph}_2)_2$ and $\text{Os}_3(\text{CO})_8(\text{C}_2\text{Me}_2)_2$ were previously prepared by a similar method. Johnson, B. F. G.; Khattar, R.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1987**, 319, C51.

Figure 1. Molecular structure of **4**. Selected bond distances (Å): Os(1)–Os(2) = 2.7515(9), Os(1)–Os(3) = 2.6952(8), Os(2)–Os(3) = 2.6942(5), Os(1)–C(9) = 2.189(7), Os(1)–C(23) = 2.196(7), Os(2)–C(24) = 2.175(8), Os(2)–C(10) = 2.201(7), Os(3)–C(9) = 2.136(8), Os(3)–C(10) = 2.118(7), Os(3)–C(23) = 2.128(7), Os(3)–C(24) = 2.137(7), C(9)–C(10) = 1.42(1), C(23)–C(24) = 1.41(1), C(16)–C(17) = 1.18(2), C(30)–C(31) = 1.17(1). Selected bond angles (deg): Os(1)–Os(2)–Os(3) = 59.32(2), Os(3)–Os(1)–Os(2) = 59.28(2), C(9)–Os(1)–C(23) = 100.8(3), C(9)–Os(3)–C(10) = 39.0(3), C(10)–Os(2)–C(24) = 100.7(3), C(23)–Os(3)–C(24) = 38.5(3), C(10)–C(9)–C(22) = 124.8(7), C(9)–C(10)–C(11) = 126.6(6), C(24)–C(23)–C(36) = 127.1(7), C(23)–C(24)–C(25) = 123.3(7).

Scheme 1

benzene⁷ ligand η^6 -bonded to a Os(CO)₂ group. Although compound **4** has no crystallographically imposed symmetry in the solid state, it exhibits the expected idealized C_{2v} symmetry in solution, such that the ¹³C NMR spectrum displays three resonance signals in a 1:2:1 ratio for the eight carbonyl carbons and seven resonance signals for the 28 ring carbons. The coordinated and free C≡C carbon resonances appearing at δ 167.2 and 80.5 are comparable with those recorded for **1**. The methylene carbon resonances in the range δ 52.6–18.1 can be assigned (Figure 2) on the basis of a 2D-HSQC experi-

ment,⁸ while the methylene protons are assigned according to an H,H-COSY experiment.

Since compound **2** contains two open Os₃ faces, it reacts with Me₃NO/NCMe and C₁₄H₂₀ to produce the double-decker tris(cyclodiyne) complex (Os₃(CO)₈)₂(μ_3 , μ_3 - η^2 , η^2 -C₁₄H₂₀)(μ_3 - η^2 -C₁₄H₂₀)₂ (**5**) in 28% yield. Alternatively, sequential treatment of **1** with Me₃NO/NCMe and compound **4** also leads to **5**. Compound **5** is analogous to **4** but with two Os₃ spacers. Two isomers in an approximate ratio of 5:1 are present for **5**, where the alkyne–osmium π bonds can lie on the same side (*syn*) or opposite sides (*anti*) of the bridging carbocycle. The ¹³C NMR data of **5** (the major species) are consistent

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Figure 2. 2D $^{13}\text{C}/^1\text{H}$ shift correlation spectrum of **4**, taken in CDCl_3 at 23 $^\circ\text{C}$.

with C_{2h} symmetry (*anti*-form) or C_{2v} symmetry (*syn*-form) in solution, showing a signal at δ 80.5 for the free alkyne carbons, two signals at δ 167.8 and 165.9 for the coordinated alkyne carbons, and eight discrete signals

in the range δ 52.6–18.2 for the methylene carbons. Efforts to grow suitable crystals for an X-ray diffraction study failed. Since compound **2** was structurally characterized as having an *anti*-configuration,⁵ it seems reasonable to assume that the *anti*-form is dominant for **5**.

Compound **3** was previously obtained from photoirradiation of **1** in the presence of a $\text{C}_{14}\text{H}_{20}$ ligand.⁵ Likewise, co-irradiation of **1** and **3** produces the double-decker bis(osmacyclopentadiene) complex $(\text{Os}_3(\text{CO})_9)_2-(\mu,\mu-\eta^4,\eta^4-(\text{C}_{14}\text{H}_{20})_3)$ (**6**). A convenient method to make **6** is irradiation of **2** and $\text{C}_{14}\text{H}_{20}$ by inserting one cyclodiyne into each Os_3 framework. The IR spectra of **6** and **3** suggest similar coordination environments for the two complexes. However, four geometric isomers can result for **6**, in which the two osmium atoms of the metallacycles can be *cis* or *trans* to one another, and the two osmium atoms above the metallacycles can lie on the same side (*syn*) or opposite sides (*anti*). Two major products, **6a** and **6b**, in about equal amounts have been isolated, which present the same blue color and compatible mass, IR, and NMR data.

The ORTEP diagram of **6b** (Figure 3) exhibits a *trans-syn* configuration, where the two Os_3 clusters adopt the same environment. The Os–Os distances in each cluster show substantial variation, ranging from 2.7229(6) to 2.9293(6) Å. The two osmacyclopentadiene fragments form σ bonds to Os(1) and Os(4) and π bonds to Os(2) and Os(5) atoms. Each osmacyclopentadiene ring is

Figure 3. Molecular structure of **6b**. Selected bond distances (Å): Os(1)–Os(2) = 2.7428(5), Os(1)–Os(3) = 2.9293(6), Os(2)–Os(3) = 2.7229(6), Os(4)–Os(5) = 2.7414(6), Os(4)–Os(6) = 2.9254(6), Os(5)–Os(6) = 2.7254(6), Os(2)–C(19) = 2.254(9), Os(2)–C(20) = 2.259(9), Os(2)–C(33) = 2.273(9), Os(2)–C(34) = 2.238(9), Os(5)–C(40) = 2.292(9), Os(5)–C(41) = 2.255(9), Os(5)–C(47) = 2.281(9), Os(5)–C(48) = 2.271(9), Os(1)–C(19) = 2.135(9), C(19)–C(20) = 1.43(1), C(20)–C(33) = 1.46(1), C(33)–C(34) = 1.41(1), Os(1)–C(34) = 2.140(9), Os(4)–C(48) = 2.137(9), C(47)–C(48) = 1.43(1), C(40)–C(47) = 1.45(1), C(40)–C(41) = 1.43(1), Os(4)–C(41) = 2.159(9). Selected bond angles (deg): Os(1)–Os(2)–Os(3) = 64.82(2), Os(1)–Os(3)–Os(2) = 57.92(1), Os(4)–Os(5)–Os(6) = 64.70(2), Os(4)–Os(6)–Os(5) = 57.91(1), C(20)–C(19)–Os(1) = 116.2(7), C(19)–C(20)–C(33) = 114.2(8), C(34)–C(33)–C(20) = 115.5(9), C(33)–C(34)–Os(1) = 116.2(7), C(19)–Os(1)–C(34) = 76.7(4), C(47)–C(48)–Os(4) = 116.2(6), C(40)–C(47)–C(48) = 115.2(8), C(41)–C(40)–C(47) = 115.2(8), C(40)–C(41)–Os(4) = 115.5(6), C(48)–Os(4)–C(41) = 76.8(4).

Figure 4. Molecular structure of **6a**. Selected bond distances (Å): Os(1)–Os(2) = 2.7444(7), Os(1)–Os(3) = 2.9142(7), Os(2)–Os(3) = 2.7265(6), Os(4)–Os(5) = 2.7389(6), Os(4)–Os(6) = 2.7128(6), Os(5)–Os(6) = 2.9015(6), Os(2)–C(19) = 2.258(13), Os(2)–C(20) = 2.28(1), Os(2)–C(33) = 2.28(1), Os(2)–C(34) = 2.24(1), Os(4)–C(40) = 2.264(9), Os(4)–C(41) = 2.28(1), Os(4)–C(47) = 2.28(1), Os(4)–C(48) = 2.291(1), Os(1)–C(19) = 2.13(1), Os(1)–C(34) = 2.14(1), C(19)–C(20) = 1.44(1), C(20)–C(33) = 1.46(2), C(33)–C(34) = 1.42(1), Os(5)–C(40) = 2.12(1), Os(5)–C(47) = 2.13(1), C(40)–C(41) = 1.45(1), C(41)–C(48) = 1.42(2), C(47)–C(48) = 1.46(1). Selected bond angles (deg): Os(1)–Os(2)–Os(3) = 64.37(2), Os(1)–Os(3)–Os(2) = 58.11(2), Os(4)–Os(5)–Os(6) = 57.41(2), Os(4)–Os(6)–Os(5) = 58.28(1), C(20)–C(19)–Os(1) = 116.5(8), C(19)–C(20)–C(33) = 113.4(9), C(34)–C(33)–C(20) = 116.2(9), C(33)–C(34)–Os(1) = 115.2(8), C(19)–Os(1)–C(34) = 77.2(4), C(48)–C(47)–Os(5) = 114.6(8), C(41)–C(48)–C(47) = 116.3(9), C(48)–C(41)–C(40) = 114.4(9), C(41)–C(40)–Os(5) = 116.3(8), C(40)–Os(5)–C(47) = 77.6(4).

nearly planar, and the interplane angle between the two rings is 54°, leading to a bowl-like shape for the polycyclic chain. On the other hand, the molecular structure of **6a** displays a *cis-anti* configuration. A striking feature about **6a** is the polycyclic chain which is annealed into a helix. The crystalline material of **6a** is achiral, with each unit cell containing a right- and a left-handed helical molecule. The ORTEP diagram for the left-handed enantiomer is exhibited in Figure 4, which displays interatomic distances and angles similar to **6b**. Stereoscopic views of **6a** and **6b** are provided in Figure 5 for comparison. The remaining two isomers are probably among the several uncharacterized minor products (<1%). We do not have mechanistic information to account for the product distribution. However, the energy-minimized structures constructed for the *trans-anti* and *cis-syn* forms appear more space-congested than the corresponding *cis-anti* (**6a**) and *trans-syn* (**6b**) forms, suggesting that steric effects might play an importance role.

Compounds **3**, **4**, **5**, and **6** are air-stable and soluble in common organic solvents. They contain two pendant alkyne groups and can be viewed as metalated polycyclodiyne with 29, 30, 46, and 44 ring atoms, respectively. The distances between the two alkynes are diverse, ranging from 8.8 to 24 Å (Chart 1). The three carbocyclic rings of **5** are presumed to line up as in **4**, giving an estimated alkyne–alkyne distance of 24 Å,

while the curled bonding feature of **6** leads to shorter alkyne–alkyne spans, being 16.8 Å for **6a** and 12.4 Å for **6b**.

In conclusion, the synthesis of **3–6** is of interest within the context of the chemistry of cyclodiyne and metallacycles and the ability of a cluster system to promote these reactions. It appears that the multicuster complexes $(C_{14}H_{20})[Os_3(C_{14}H_{20})]_n$ ($n \geq 2$) containing a straight or a curled metallapolycyclodiyne chain can be prepared by repeating the $Me_3NO/MeCN$ treatment or photoirradiation with or without the presence of $C_{14}H_{20}$ ligands. Moreover, the flexibility of the terminal cycloene units should provide the possibility of a metal-induced ring closure to form macrocyclic compounds,⁹ which are important topics in supramolecular chemistry.¹⁰ Further investigation is in progress in our laboratory.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques.¹¹ Cyclotradeca-1,8-diyne ($C_{14}H_{20}$)¹² and $Os_3(CO)_{10}$

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Figure 5. Stereoscopic views of **6a** and **6b**.

Table 1. Crystallographic Data for **4**, **6a**, and **6b**

	4	6a	6b
chem formula	C ₃₆ H ₄₀ O ₈ Os ₃	C ₆₀ H ₆₀ O ₁₈ Os ₆	C ₆₀ H ₆₀ O ₁₈ Os ₆
cryst solvent	1/2 C ₁₄ H ₂₀	C ₆ H ₆	C ₇ H ₁₆
cryst syst	triclinic	triclinic	monoclinic
fw	1263.41	2288.39	2310.48
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.444(3)	13.1256(6)	18.738(1)
<i>b</i> , Å	15.579(2)	15.8922(7)	19.762(1)
<i>c</i> , Å	16.107(2)	18.1694(8)	18.943(1)
α , deg	115.50(2)	111.879(1)	90
β , deg	92.03(2)	94.876(1)	96.231(2)
γ , deg	96.30(2)	99.070(1)	90
<i>V</i> , Å ³	2117.0(8)	3430.1(3)	6973.0(9)
<i>Z</i>	2	2	4
<i>D</i> _{calc} , g cm ⁻³	1.982	2.216	2.201
μ , mm ⁻¹	9.03	11.136	10.957
<i>R</i> ₁ / <i>R</i> _w ^{2a}	0.0408/0.1099	0.0523/0.1085	0.0465/0.0885
GO _F on <i>F</i> ²	1.064	1.003	1.001

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; R_{w2} = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum w|F_o|^4 \}^{1/2}.$$

(NCMe)₂¹³ were prepared by literature methods. Anhydrous trimethylamine *N*-oxide was obtained from Me₃NO·2H₂O (98%, Aldrich) by sublimation at 110 °C under vacuum. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use.¹⁴ Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). 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 JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Preparation of 4. Compound **1** (50 mg, 0.048 mmol) and C₁₄H₂₀ (23 mg, 0.12 mmol) were dissolved in CH₂Cl₂ (25 mL), and Me₃NO (7 mg, 0.096 mmol) dissolved in MeCN (8 mL) was added dropwise over 1 h. The resulting solution was stirred at ambient temperature for 3.5 h. The solvents were removed on a rotary evaporator, and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane as eluant (1:9, v/v). Crystallization of the material forming the major yellow band from *n*-heptane at -15 °C afforded orange-yellow needle crystals of Os₃(CO)₈(μ₃-η²-C₁₄H₂₀)₂ (**4**; 18 mg, 32%). Mass spectrum (FAB): *m/z* 1170 (M⁺, ¹⁹⁰Os). IR (CH₂Cl₂, νCO): 2080 (m), 2040 (s), 2016 (sh), 2000 (vs), 1970 (m), 1936 (w) cm⁻¹. ¹H NMR (CDCl₃, 23 °C): δ 3.59, 3.46, 2.28, 2.11, 1.72, 1.51 (m, CH₂). ¹³C{¹H} NMR (CDCl₃, 23 °C): δ 181.2 (CO), 178.8 (CO), 167.2 (C≡C-Os), 166.0 (CO), 80.5 (free C≡C), 52.6, 34.1, 28.6, 26.4, 18.1 (CH₂). Anal. Calcd for C₃₆H₄₀O₈Os₃: C, 36.90; H, 3.40. Found: C, 36.71; H, 3.49.

Preparation of 5 from 2 and C₁₄H₂₀. Compound **2** (10 mg, 0.005 mmol) and C₁₄H₂₀ (8 mg, 0.04 mmol) were dissolved in CH₂Cl₂ (5 mL), and a solution of Me₃NO (2 mg, 0.03 mmol) in MeCN (2 mL) was added via a syringe over 1 h. The resulting mixture was stirred for another 3 h at ambient temperature. The solvents were removed on a rotary evaporator, and the residue was subjected to TLC, with CH₂Cl₂/*n*-hexane as eluant (2:3, v/v). The first yellow band was isolated and characterized as Os₃(CO)₈(μ₃-η²-C₁₄H₂₀)(μ₃-η²-C₁₄H₂₀)₂ (**5**; 3 mg, 28%). Mass spectrum (FAB): *m/z* 2152 (M⁺, ¹⁹⁰Os). IR (CH₂Cl₂, νCO): 2080 (m), 2036 (s), 2016 (sh), 1998 (vs), 1968 (m), 1934 (w) cm⁻¹. ¹H NMR (CDCl₃, 23 °C): δ 3.71 (m, 4H), 3.61 (m, 4H), 3.39 (m, 8H), 2.29 (m, 8H), 2.13 (m, 4H), 1.94 (m, 4H), 1.77 (m, 24H), 1.50 (m, 4H). ¹³C{¹H} NMR (CDCl₃, 23 °C): δ 181.2 (CO), 178.9 (CO), 178.6 (CO), 167.8, 165.9 (C≡C-Os₃(CO)₈), 165.5 (CO), 80.5 (free C≡C), 52.6, 48.6, 34.4, 32.4, 28.7, 27.5, 26.4, 18.2 (CH₂). Anal. Calcd for C₅₈H₆₀O₁₆Os₆: C, 32.31; H, 2.79. Found: C, 32.52; H, 2.79.

Preparation of 5 from 1 and 4. Compound **1** (10 mg, 0.01 mmol) was dissolved in CH₂Cl₂ (5 mL), and a solution of Me₃NO (1.5 mg, 0.02 mmol) in MeCN (2 mL) was added over 1 h. The solution was stirred for another 3 h at ambient temperature. Compound **4** (17 mg, 0.015 mmol) was added into the solution, and the resulting mixture was stirred for 2 h. The solvent was removed on a rotary evaporator, and the residue was subjected to TLC. Compound **5** (4 mg, 19%) was obtained from the second yellow band, and the unconsumed **4** (5 mg) was recovered from the first yellow band.

Preparation of 6 from 2 and C₁₄H₂₀. 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. Compound **2** (50 mg, 0.026 mmol) and C₁₄H₂₀ (65 mg, 0.35 mmol) were dissolved in THF (35 mL). The mixture was irradiated for 2.5 h with dinitrogen slowly bubbling through the solution. The solvent was removed on a rotary evaporator, and the residue was subjected to TLC, eluting with CH₂Cl₂/*n*-hexane (1:4, v/v). Two blue bands were isolated to give **6a** (5 mg, 9%) and **6b** (5 mg, 9%), which have the same chemical formula of Os₃(CO)₉(μ₄-η⁴-C₁₄H₂₀)₃.

Characterization of 6a. Mass spectrum (FAB): *m/z* 2212. IR (CH₂Cl₂, νCO): 2100 (m), 2048 (vs), 2012 (sh), 1998 (vs), 1964 (s), 1916 (m) cm⁻¹. ¹H NMR (C₆D₆, 23 °C): δ 3.47 (m), 3.36 (m), 3.23 (m), 3.09 (m), 2.93 (m), 2.57 (m), 2.32 (m), 2.21–0.90 (m). ¹³C{¹H} NMR (C₆D₆, 23 °C): δ 177.9, 176.1, 176.0 (CO), 175.8, 161.8, 130.8, 127.1 (μ-C₄Os), 82.5, 80.1 (free C≡C), 44.8, 42.9, 36.4, 34.0, 32.8, 31.6, 31.1, 30.6, 29.9, 28.8, 28.3, 27.5, 26.7, 25.0, 19.5, 17.7 (CH₂).

Characterization of 6b. Mass spectrum (FAB): *m/z* 2212. IR (CH₂Cl₂, νCO): 2100 (m), 2048 (vs), 2012 (sh), 1998 (vs),

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Chart 1

1964 (s), 1916 (m) cm^{-1} . ^1H NMR (CD_2Cl_2 , 23 $^\circ\text{C}$): δ 3.29 (m), 3.05 (m), 2.84 (m), 2.61 (m), 2.45 (m), 2.32 (m), 2.22 (m), 2.14–0.85 (m). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23 $^\circ\text{C}$): δ 178.0, 176.1, 175.9 (CO), 175.8, 161.4, 130.5, 127.1 ($\mu\text{-C}_4\text{Os}$), 82.1, 80.2 (free C $\equiv$ C), 44.7, 42.3, 36.0, 33.6, 32.2, 31.4, 31.1, 29.4, 28.7, 28.5, 27.7, 26.7, 25.3, 19.3, 17.6 (CH_2).

Preparation of 6 from 1 and 3. This reaction was carried out in the same vessel described above. Compounds **1** (20 mg, 0.019 mmol) and **3** (23 mg, 0.019 mmol) were dissolved in *n*-hexane (20 mL). The mixture was irradiated for 2.5 h with dinitrogen slowly bubbling through the solution. The solvent was removed on a rotary evaporator, and the residue separated by TLC. Compounds **6a** (3 mg, 7%) and **6b** (3 mg) were obtained.

Structure Determination for 4, 6a, and 6b. The crystals of **4**, **6a**, and **6b** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on Nonius CAD-4 (for **4**) and Bruker Smart ApexCCD (for **6a** and **6b**) diffractometers with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The θ range for data collection was 1.41–27.50 $^\circ$ for **4**, 1.22–27.50 $^\circ$ for **6a**, and 1.09–27.50 $^\circ$ for **6b**. Of the 9721, 37 903, and 57 997 reflections collected for **4**, **6a**,

and **6b**, 9721, 15 690, and 16 011 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.¹⁵ The data collection and refinement parameters are presented in Table 1.

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

Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond angles, bond distances, and torsion angles of **4**, **6a**, and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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