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# Syntheses of Beltlike Polycyclodiynes Intercalated with Triosmium Carbonyl Clusters

Wen-Yann Yeh* and Tsun-Wei Shiue

*Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 804*

Shie-Ming Peng and Gene-Hsiang Lee

*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106*

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The bis(cyclodiyne) complex $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**4**) has been prepared by treating $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) with $Me_3NO$ in the presence of cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) ligand. Thermolysis of **4** leads to the osmacyclopentadiene complex $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}(C_{14}H_{20})_2)$ (**3**). The tris(cyclodiyne) complex $(Os_3(CO)_8)_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**5**) is obtained from the reaction of $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) with $Me_3NO$ and $C_{14}H_{20}$, while photoirradiation of **2** and $C_{14}H_{20}$ affords the bis(osmacyclopentadiene) complex $(Os_3(CO)_9)_2\text{-}(\mu,\mu\text{-}\eta,^4\eta^4\text{-}(C_{14}H_{20})_3)$ (**6**). Co-irradiation of **3** and **1** also produces **6**. Compounds **3**, **4**, **5**, and **6** can be viewed as cluster-intercalated, beltlike polycyclodiynes. The structures of **4** and **6** (two isomers) have been determined by an X-ray diffraction study.

## Introduction

Cyclic dialkynes (or cyclodiynes)[1] 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 ($C_{14}H_{20}$) complexes $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**), $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**), and $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}(C_{14}H_{20})_2)$ (**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 polycyclodiynes **4**−**6**. The reaction pathways are outlined in Scheme 1.

## Results and Discussion

To a mixture of **1** and $C_{14}H_{20}$ in dichloromethane was added 2 equiv of $Me_3NO$ (to remove CO) in MeCN at room temperature to generate the bis(cyclodiyne) complex $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**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 $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$.[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 Os(1)−Os(2) distance is significantly longer than the other two intermetallic distances. The Os(1) and Os(2) atoms are each associated with three terminal carbonyl ligands, while the Os(3) atom is linked with two. The alkyne C(9)−C(10) and C(23)−C(24) units are asymmetrically bonded to the osmium atoms, formally forming $\pi$ bonds to the Os(3) atom and $\sigma$ bonds to the Os(1) and Os(2) atoms. The atoms (C(9), C(10), Os(1), and Os(2)) and the atoms (C(23), C(24), Os(1), and Os(2)) are coplanar to within 0.1 Å, and the dihedral angle between the two planes is 108°. Thus, the $[C_4Os_2]$ fragment may also be described as a diosma-Dewar-

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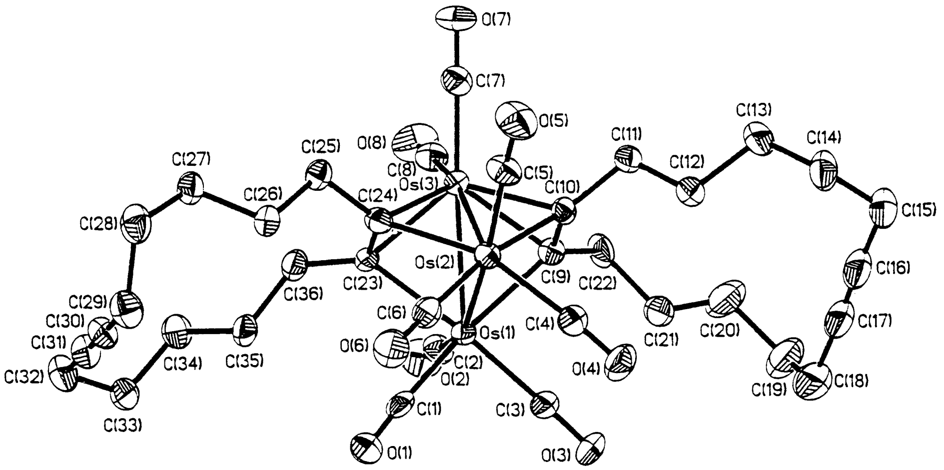
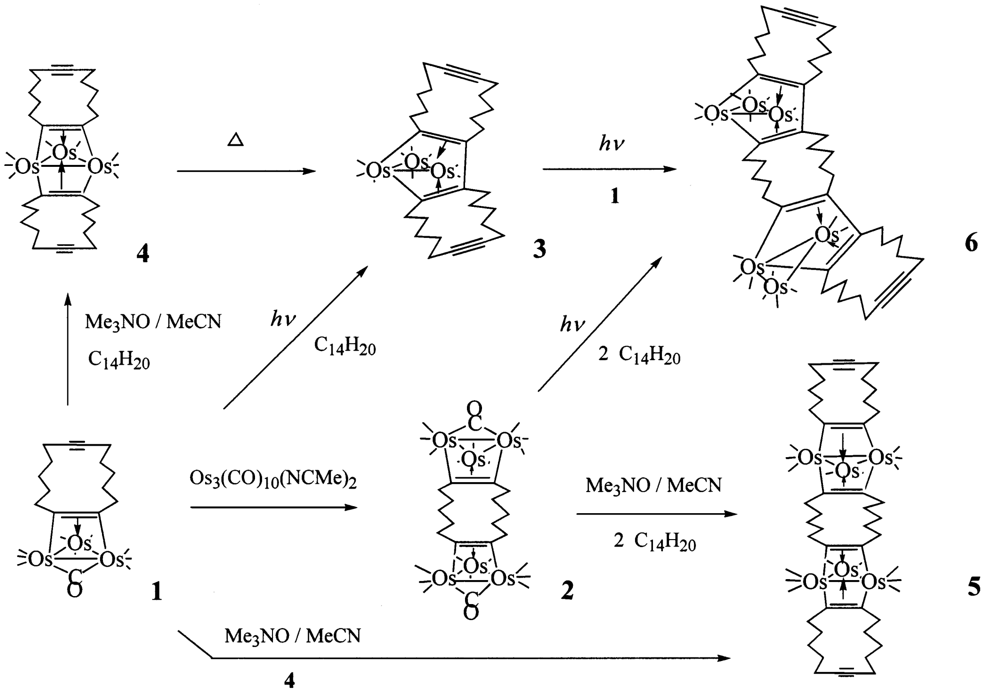


**Figure 1.** Molecular structure of **4**. Selected bond distances (Å): Os(1)−Os(2) = 2.7515(9), Os(1)−Os(3) = 2.6952(8), Os(2)−Os(3) = 2.6942(5), Os(1)−C(9) = 2.189(7), Os(1)−C(23) = 2.196(7), Os(2)−C(24) = 2.175(8), Os(2)−C(10) = 2.201(7), Os(3)−C(9) = 2.136(8), Os(3)−C(10) = 2.118(7), Os(3)−C(23) = 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**



benzene[7] ligand $\eta^6$-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 $^{13}C$ 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 $\delta$ 167.2 and 80.5 are comparable with those recorded for **1**. The methylene carbon resonances in the range $\delta$ 52.6−18.1 can be assigned (Figure 2) on the basis of a 2D-HSQC experiment,[8] while the methylene protons are assigned according to an H,H-COSY experiment.

Since compound **2** contains two open $Os_3$ faces, it reacts with $Me_3NO/NCMe$ and $C_{14}H_{20}$ to produce the double-decker tris(cyclodiyne) complex $(Os_3(CO)_8)_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**5**) in 28% yield. Alternatively, sequential treatment of **1** with $Me_3NO/NCMe$ and compound **4** also leads to **5**. Compound **5** is analogous to **4** but with two $Os_3$ spacers. Two isomers in an approximate ratio of 5:1 are present for **5**, where the alkyne−osmium $\pi$ bonds can lie on the same side (*syn*) or opposite sides (*anti*) of the bridging carbocycle. The $^{13}C$ NMR data of **5** (the major species) are consistent

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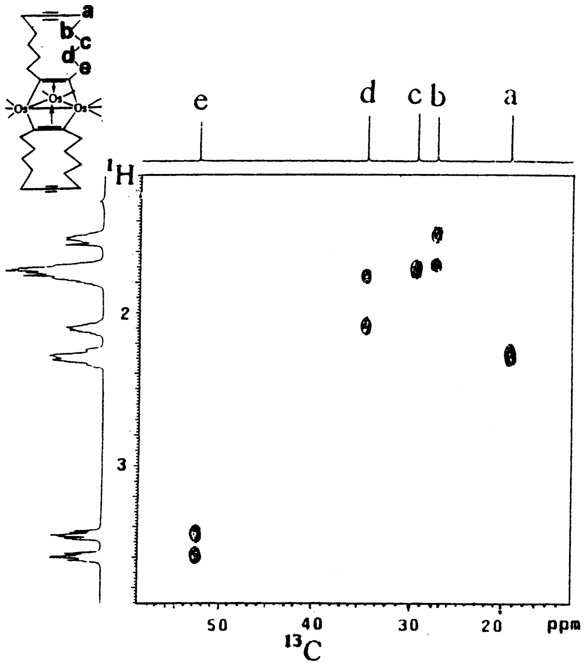

**Figure 2.** 2D $^{13}C/^{1}H$ shift correlation spectrum of **4**, taken in $CDCl_3$ at 23 °C.

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 $C_{14}H_{20}$ ligand.[5] Likewise, co-irradiation of **1** and **3** produces the double-decker bis(osmacyclopentadiene) complex $(Os_3(CO)_9)_2$-$(\mu,\mu\text{-}\eta,^4\eta^4\text{-}(C_{14}H_{20})_3)$ (**6**). A convenient method to make **6** is irradiation of **2** and $C_{14}H_{20}$ 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

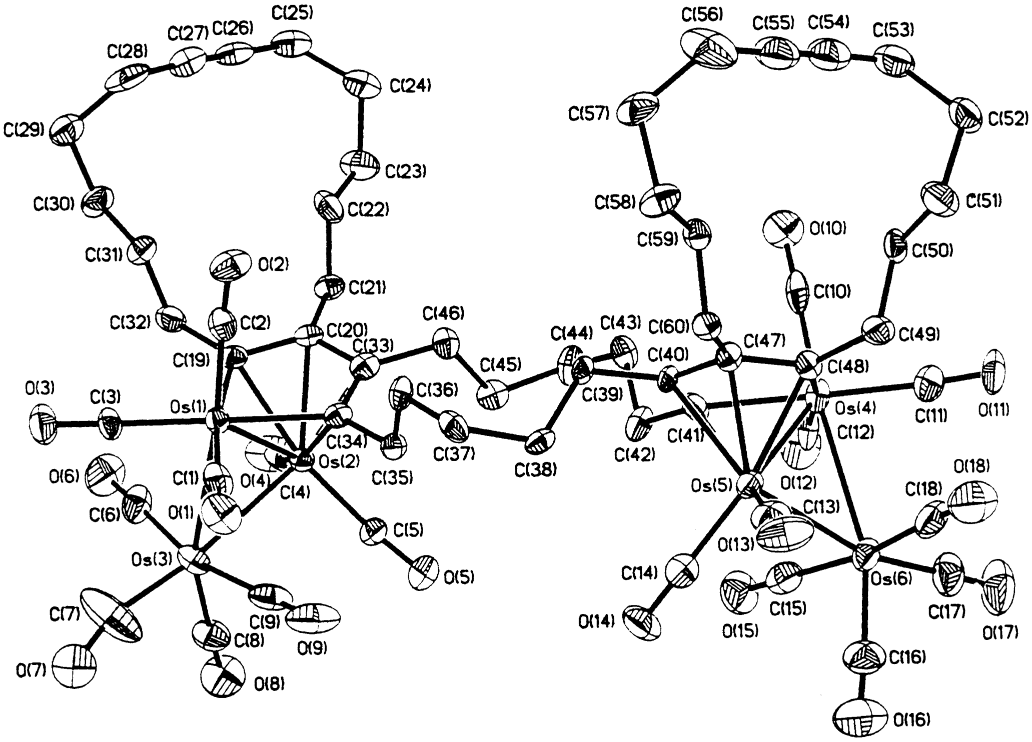

**Figure 3.** Molecular structure of **6b**. Selected bond distances (Å): Os(1)−Os(2) = 2.7428(5), Os(1)−Os(3) = 2.9293(6), Os(2)−Os(3) = 2.7229(6), Os(4)−Os(5) = 2.7414(6), Os(4)−Os(6) = 2.9254(6), Os(5)−Os(6) = 2.7254(6), Os(2)−C(19) = 2.254(9), Os(2)−C(20) = 2.259(9), Os(2)−C(33) = 2.273(9), Os(2)−C(34) = 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).

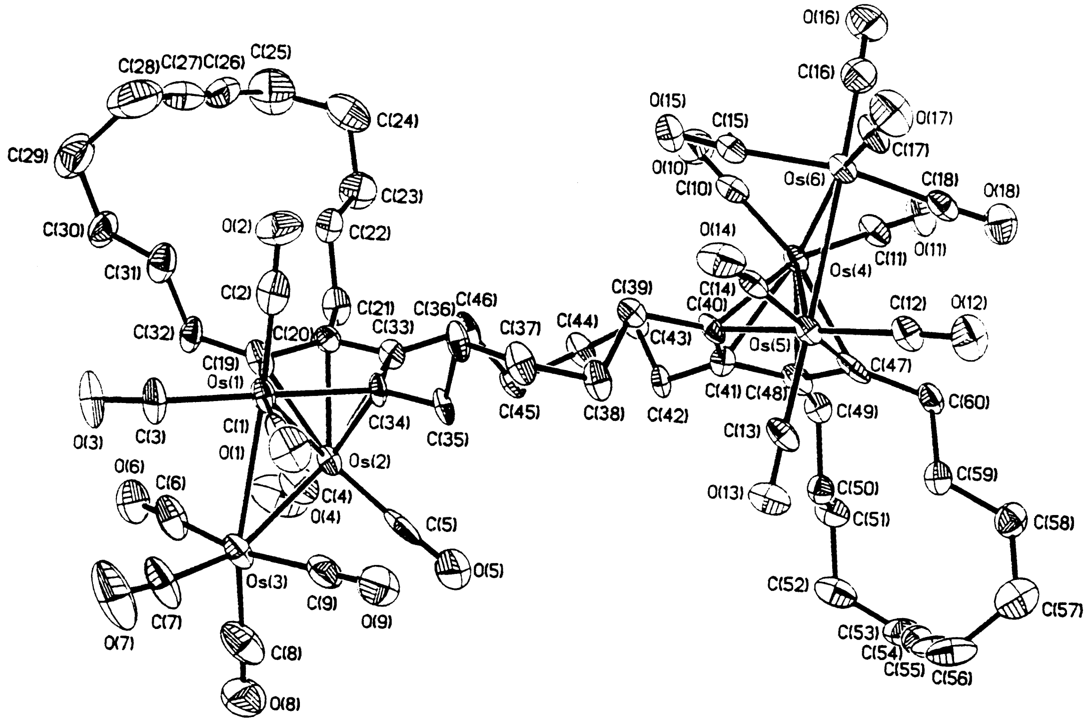

**Figure 4.** Molecular structure of **6a**. Selected bond distances (Å): Os(1)–Os(2) = 2.7444(7), Os(1)–Os(3) = 2.9142(7), Os(2)–Os(3) = 2.7265(6), Os(4)–Os(5) = 2.7389(6), Os(4)–Os(6) = 2.7128(6), Os(5)–Os(6) = 2.9015(6), Os(2)–C(19) = 2.258(13), Os(2)–C(20) = 2.28(1), Os(2)–C(33) = 2.28(1), Os(2)–C(34) = 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 bowlike 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 polycyclodiynes 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 cyclodiynes and metallacycles and the ability of a cluster system to promote these reactions. It appears that the multicluster 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 cycloyne 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] Cycloteradeca-1,8-diyne ($C_{14}H_{20}$)[12] and $Os_3(CO)_{10}$-

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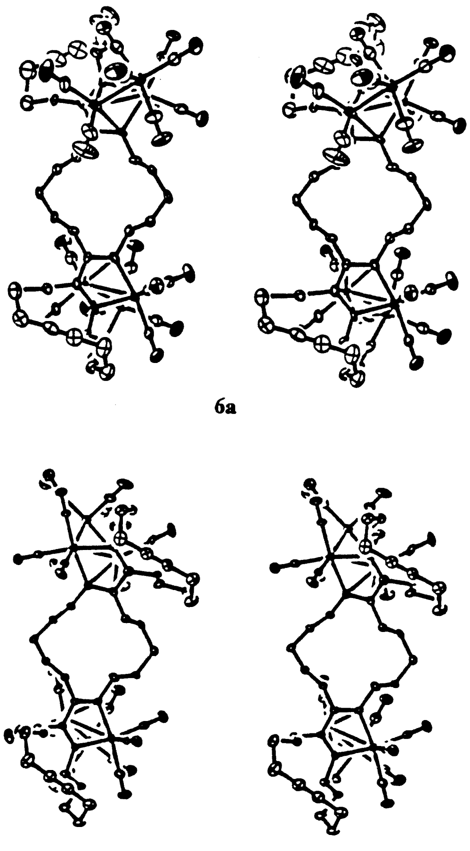

**6a**

**6b**

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

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

| | 4 | 6a | 6b |
|---|---|---|---|
| chem formula | $C_{36}H_{40}O_8Os_3$ | $C_{60}H_{60}O_{18}Os_6$ | $C_{60}H_{60}O_{18}Os_6$ |
| cryst solvent | 1/2 $C_{14}H_{20}$ | $C_6H_6$ | $C_7H_{16}$ |
| cryst syst | triclinic | triclinic | monoclinic |
| fw | 1263.41 | 2288.39 | 2310.48 |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| $a$, Å | 9.444(3) | 13.1256(6) | 18.738(1) |
| $b$, Å | 15.579(2) | 15.8922(7) | 19.762(1) |
| $c$, Å | 16.107(2) | 18.1694(8) | 18.943(1) |
| α, deg | 115.50(2) | 111.879(1) | 90 |
| $\beta$, deg | 92.03(2) | 94.876(1) | 96.231(2) |
| $\gamma$, deg | 96.30(2) | 99.070(1) | 90 |
| $V$, Å$^3$ | 2117.0(8) | 3430.1(3) | 6973.0(9) |
| $Z$ | 2 | 2 | 4 |
| $D_{calc}$, g cm$^{-1}$ | 1.982 | 2.216 | 2.201 |
| $\mu$, mm$^{-1}$ | 9.03 | 11.136 | 10.957 |
| $R_1/R_{w2}$[a] | 0.0408/0.1099 | 0.0523/0.1085 | 0.0465/0.0885 |
| GOF on $F^2$ | 1.064 | 1.003 | 1.001 |

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

$(NCMe)_2$[13] were prepared by literature methods. Anhydrous trimethylamine *N*-oxide was obtained from $Me_3NO·2H_2O$ (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 $^{13}C$ 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 $C_{14}H_{20}$ (23 mg, 0.12 mmol) were dissolved in $CH_2Cl_2$ (25 mL), and $Me_3NO$ (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 $CH_2Cl_2$/*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 $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**4**; 18 mg, 32%). Mass spectrum (FAB): *m*/*z* 1170 (M$^+$, $^{190}$Os). IR ($CH_2Cl_2$, $\nu$CO): 2080 (m), 2040 (s), 2016 (sh), 2000 (vs), 1970 (m), 1936 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 23 °C): $\delta$ 3.59, 3.46, 2.28, 2.11, 1.72, 1.51 (m, $CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C): $\delta$ 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 ($CH_2$). Anal. Calcd for $C_{36}H_{40}O_8Os_3$: C, 36.90; H, 3.40. Found: C, 36.71; H, 3.49.

**Preparation of 5 from 2 and $C_{14}H_{20}$.** Compound **2** (10 mg, 0.005 mmol) and $C_{14}H_{20}$ (8 mg, 0.04 mmol) were dissolved in $CH_2Cl_2$ (5 mL), and a solution of $Me_3NO$ (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 $CH_2Cl_2$/*n*-hexane as eluant (2:3, v/v). The first yellow band was isolated and characterized as $(Os_3(CO)_8)_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})_2$ (**5**; 3 mg, 28%). Mass spectrum (FAB): *m*/*z* 2152 (M$^+$, $^{190}$Os). IR ($CH_2Cl_2$, $\nu$CO): 2080 (m), 2036 (s), 2016 (sh), 1998 (vs), 1968 (m), 1934 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 23 °C): $\delta$ 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C): $\delta$ 181.2 (CO), 178.9 (CO), 178.6 (CO), 167.8, 165.9 (C≡C−$Os_3$-$(CO)_8$), 165.5(CO), 80.5 (free C≡C), 52.6, 48.6, 34.4, 32.4, 28.7, 27.5, 26.4, 18.2 ($CH_2$). Anal. Calcd for $C_{58}H_{60}O_{16}Os_6$: 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 $CH_2Cl_2$ (5 mL), and a solution of $Me_3NO$ (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 separated by 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 $C_{14}H_{20}$.** 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 $C_{14}H_{20}$ (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 $CH_2Cl_2$/*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 $(Os_3(CO)_9)_2(\mu,\mu\text{-}\eta,^4\eta^4\text{-}(C_{14}H_{20})_3)$.

**Characterization of 6a.** Mass spectrum (FAB): *m*/*z* 2212. IR ($CH_2Cl_2$, $\nu$CO): 2100 (m), 2048 (vs), 2012 (sh), 1998 (vs), 1964 (s), 1916 (m) cm$^{-1}$. $^1H$ NMR ($C_6D_6$, 23 °C): $\delta$ 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). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 23 °C): $\delta$ 177.9, 176.1, 176.0 (CO), 175.8, 161.8, 130.8, 127.1 ($\mu$-$C_4$Os), 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 ($CH_2$).

**Characterization of 6b.** Mass spectrum (FAB): *m*/*z* 2212. IR ($CH_2Cl_2$, $\nu$CO): 2100 (m), 2048 (vs), 2012 (sh), 1998 (vs),

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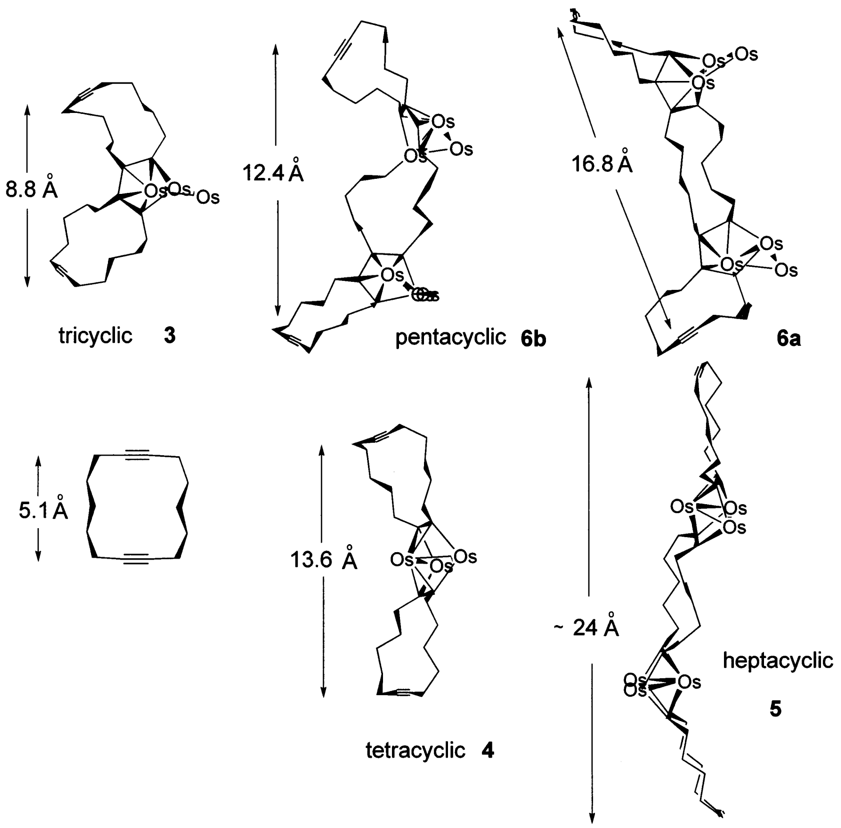
**Chart 1**



tricyclic **3** pentacyclic **6b** **6a** tetracyclic **4** heptacyclic **5**

1964 (s), 1916 (m) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 23 °C): $\delta$ 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). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 23 °C): $\delta$ 178.0, 176.1, 175.9 (CO), 175.8, 161.4, 130.5, 127.1 ($\mu$-$C_4Os$), 82.1, 80.2 (free C≡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 Kα radiation ($\lambda = 0.71073$ Å). The $\theta$ range for data collection was 1.41–27.50° for **4**, 1.22–27.50° for **6a**, and 1.09–27.50° 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.

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**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.

OM030179X

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