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C–H versus C–C Activation of Biphenylene in Its Reactions with Iron Group Carbonyl Clusters

Wen-Yann Yeh* and Sodio C. N. Hsu

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 107

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Co-thermolysis of biphenylene ((C₆H₄)₂) with Fe₃(CO)₁₂ or Fe₂(CO)₉ leads to activation of a biphenylene C–C bond to generate Fe₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂) (**1**). Similar reaction with Ru₃(CO)₁₂ affords Ru₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂) (**2**) and Ru₆(CO)₁₇(μ₆-C) (**3**), and the reaction with Os₃(CO)₁₂ affords Os₂(CO)₆(μ-η²,η⁴-(C₆H₄)₂) (**4**) and Os₄(CO)₁₂(μ₄-η²-(C₆H₃)Ph) (**5**). In contrast, treating biphenylene with Os₃(CO)₁₀(NCMe)₂ leads to C–H bond activation to give (μ-H)₂Os₃(CO)₉(μ₃-η²-C₆H₂(C₆H₄)) (**6**). The new compounds have been characterized by elemental analyses and mass, IR, and NMR spectroscopy. The structures of **2**, **4**, and **5** were determined by an X-ray diffraction study. Compound **2** and **4** can be viewed to contain a metallacyclopentadienyl unit which binds the other metal atom in an η⁵-fashion. Compound **5** is the first butterfly cluster of the type Os₄(CO)₁₂(aryne).

Introduction

The insertion of transition-metal atoms into a carbon–carbon bond through oxidative addition is known for many type of hydrocarbons, especially strained-ring compounds and compounds which become aromatic on C–C cleavage.¹ The biphenylene ligand itself has been known for many years.² An X-ray diffraction study of biphenylene suggests that the central ring of the molecule has little delocalization.³ Theoretical calculations show that biphenylene has a relatively low resonance energy of about 15 kcal/mol,⁴ while the strain energy of the four-membered ring is high, about 63 kcal/mol.⁵ This should facilitate formation of a metallacycle when biphenylene is treated with a metal complex.

Four papers concerning activation of biphenylene by mononuclear^{6–8} and binuclear⁹ metal complexes were previously reported. However, the coordination chemistry of biphenylene with metal clusters has received little attention. We have been interested in the systematic chemistry of small organic substrates bound to transition-metal carbonyl clusters.¹⁰ Presented in this work are reactions of M₃(CO)₁₂ (M = Fe, Ru, and Os) with biphenylene, leading to several new complexes containing metallacycle and benzyne moieties.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques.¹¹ Fe₃(CO)₁₂, Fe₂(CO)₉, and Ru₃(CO)₁₂ were prepared from Strem and used as received. Os₃(CO)₁₂ was prepared from OsO₄ and CO by the literature method.¹² Biphenylene was prepared by flash vacuum pyrolysis of phthalic anhydride as described in the literature.¹³ Solvents were dried over the appropriate reagents under dinitrogen and

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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 VXR-300 spectrometer at 300 and 75.4 MHz, respectively. Fast-atom bombardment (FAB) and electron-impact (EI) mass spectra were recorded by using a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Cheng-Kung University, Tainan, Taiwan.

Reaction of Biphenylene with Fe₃(CO)₁₂. A solution of biphenylene (30 mg, 0.2 mmol) and Fe₃(CO)₁₂ (100 mg, 0.2 mmol) in *n*-heptane (20 mL) was heated to reflux under dinitrogen for 3 h. The mixture was cooled to room temperature, and the solvent was removed under vacuum. The residue was subjected to TLC, eluting with *n*-hexane. Unreacted Fe₃(CO)₁₂ and biphenylene were recovered from the front two bands. Isolation of material from the red-brown band afforded the known Fe₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂)¹⁴ (**1**) (28 mg, 0.06 mmol, 30%). IR (KBr, νCO): 2064 (m), 2024 (s), 1990 (s), 1974 (s), 1888 (m) cm⁻¹. MS (EI): *m/z* 432 (M⁺, ⁵⁶Fe), 432 – 28*n* (*n* = 1–6). ¹H NMR (CDCl₃, 20 °C): δ 7.23–7.311 (m, 4H), 7.51 (d, *J* = 8 Hz, 2H), 7.75 (d, *J* = 8 Hz, 2H).

Reaction of Biphenylene with Fe₂(CO)₉. The reaction of Fe₂(CO)₉ (80 mg, 0.22 mmol) with biphenylene (35 mg, 0.23 mmol) was carried out in refluxing cyclohexane solution (10 mL) for 5 h. Compound **1** (33 mg, 0.08 mmol) was obtained in 36% yield after purification by TLC.

Reaction of Biphenylene with Ru₃(CO)₁₂. A solution of biphenylene (28 mg, 0.18 mmol) and Ru₃(CO)₁₂ (115 mg, 0.18 mmol) in *n*-octane (20 mL) was heated to reflux for 4 h under dinitrogen. The mixture was cooled to room temperature, and the solvent was removed under vacuum. The residue was separated by TLC, eluting with *n*-hexane. Unreacted Ru₃(CO)₁₂ and biphenylene were recovered from the front two bands. The material from the orange band was the new complex Ru₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂) (**2**) (32 mg, 0.06 mmol, 33%). The last dark red band afforded the known Ru₆(CO)₁₇-(μ₆-C)¹⁵ (**3**) (26 mg, 0.02 mmol, 33% based on Ru atom). The crystals of **2** found suitable for X-ray diffraction study were grown from a concentrated hexane solution at –20 °C.

Characterization of 2. IR (*n*-hexane, νCO): 2092 (m), 2032 (vs), 2020 (s), 1980 (m), 1882 (m, μ-CO) cm⁻¹. MS (FAB): *m/z* 524 (M⁺, ¹⁰²Ru), 523 – 28*n* (*n* = 1–6). ¹H NMR (CDCl₃, 20 °C): δ 7.13 (t, *J* = 8 Hz, 2H), 7.56 (t, *J* = 8 Hz, 2H), 7.91 (d, *J* = 8 Hz, 2H), 8.34 (d, *J* = 8 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 125.5 (s), 126.0 (s), 129.9 (s), 132.4 (s), 136.7 (s), 151.6 (s), 188.9 (s, CO). Anal. Calcd for C₁₈H₈O₆-Ru₂: C, 41.39; H, 1.54. Found: C, 40.84; H, 1.88.

Characterization of 3. IR (*n*-hexane, νCO): 2068(s), 2049 (s), 2010 (sh), 1998(w), 1958 (w), 1854 (w, br) cm⁻¹. MS (EI): *m/z* 1094 (M⁺, ¹⁰²Ru) and successive loss of CO. The IR data match the literature values for the compound.¹⁵

Reaction of Biphenylene with Os₃(CO)₁₂. Biphenylene (90 mg, 0.59 mmol), Os₃(CO)₁₂ (90 mg, 0.10 mmol), and *n*-decane (1 mL) were mixed in a Teflon-sealed Schlenk tube under dinitrogen. The tube was placed in an oil bath at 200 °C for 15 h. After cooling to ambient temperature, the brown-red residue was extracted with *n*-hexane (3 × 10 mL) to give a red-brown solution. Unreacted Os₃(CO)₁₂ (30 mg, 33%) was recovered from the insoluble solids. The extractant was concentrated to ca. 5 mL on a rotary evaporator and separated by TLC with *n*-hexane as the eluant. Unreacted biphenylene was recovered from the first pale yellow band. The material from the second yellow band afforded Os₂(CO)₆(μ-η²,η⁴-(C₆H₄)₂)

(**4**) (16 mg, 0.022 mmol, 23%). The third red band gave Os₄(CO)₁₂(μ₄-η²-(C₆H₃)Ph) (**5**) (28 mg, 0.02 mmol, 30% based on Os atom). The crystals of **4** and **5** found suitable for X-ray diffraction study were each grown from a concentrated hexane solution at –20 °C.

Characterization of 4. IR (*n*-hexane, νCO): 2084 (m), 2072 (sh), 2048 (s), 2004 (s), 1996 (s), 1974 (s) cm⁻¹. MS (EI): *m/z* 704 (M⁺, ¹⁹²Os), 702 – 28*n* (*n* = 1–6). ¹H NMR (CDCl₃, 20 °C): δ 7.06 (t, *J* = 8 Hz, 2H), 7.38 (t, *J* = 8 Hz, 2H), 8.05 (d, *J* = 8 Hz, 2H), 8.37 (d, *J* = 8 Hz, 2H).

Characterization of 5. IR (*n*-hexane, νCO): 2100 (w), 2076 (s), 2044 (vs), 2008 (s), 1998 (s), 1972 (m) cm⁻¹. MS (EI): *m/z* 1256 (M⁺, ¹⁹²Os), 1256 – 28*n* (*n* = 1–12). ¹H NMR (CDCl₃, 20 °C): δ 6.32 (d, *J* = 9 Hz, 1H), 6.50 (d, *J* = 9 Hz, 1H), 7.13 (s, 1H), 7.0–7.8 (m, 5H, Ph). Anal. Calcd for C₂₄H₈O₁₂Os₄: C, 23.08; H, 0.65. Found: C, 22.88; H, 0.87.

Reaction of Biphenylene with Os₃(CO)₁₀(NCMe)₂. A mixture of biphenylene (33 mg, 0.2 mmol) and Os₃(CO)₁₀(NCMe)₂ (40 mg, 0.043 mmol) was ground and placed in a Teflon-sealed Schlenk tube under N₂. The tube was placed in an oil bath at 180 °C for 5 min and then cooled to ambient temperature. The residue was extracted with dichloromethane and subjected to TLC, with *n*-hexane as the eluant. (μ-H)₂Os₃(CO)₉(μ₃-η²-C₆H₂(C₆H₄)) (**6**) (15 mg, 0.015 mmol, 36%) was isolated from the major yellow band. IR (*n*-hexane, νCO): 2112 (m), 2084 (s), 2060 (vs), 2032 (s), 2020 (sh), 2004 (vs), 1986 (s), 1974 (w) cm⁻¹. MS (FAB): *m/z* 980 (M⁺, ¹⁹²Os), 980 – 28*n* (*n* = 1–9). ¹H NMR (CDCl₃, 20 °C): δ –18.99 (s, 2μ-H), 7.04–6.94 (m, 4H), 7.02 (s, 2H).

X-ray Crystallography. A dark orange crystal of Ru₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂) (**2**, ca. 0.20 × 0.25 × 0.35 mm), a yellow crystal of Os₂(CO)₆(μ-η²,η⁴-(C₆H₄)₂) (**4**, ca. 0.20 × 0.20 × 0.10 mm), and a dark red crystal of Os₄(CO)₁₂(μ₄-η²-(C₆H₃)Ph) (**5**, ca. 0.30 × 0.20 × 0.40 mm) were each mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Lattice parameters were determined from 25 randomly selected reflections with 2θ ranging from 23.14° to 25.86° (compound **2**), from 15.12° to 24.42° (compound **4**), and from 15.00° to 30.40° (compound **5**). The data were collected at 298 K using the θ/2θ scan technique to maximum 2θ values of 50.0° for **2**, **4**, and **5**. A scan of 2(0.65 + 0.35 tan θ)° at a variable speed of 2.06–8.24°/min for **2** and **4** and 2(0.90 + 0.35 tan θ)° at a variable speed of 3.30–8.24°/min for **5** was performed. The intensities of three representative reflections, which were measured every 60 min of X-ray exposure time, remained constant throughout data collection, so no decay correction was applied. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structures were solved by the direct method and refined by least-squares cycles.¹⁶ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the NRCSDP-VAX package. A summary of relevant crystallographic data for **2**, **4**, and **5** is provided in Table 1.

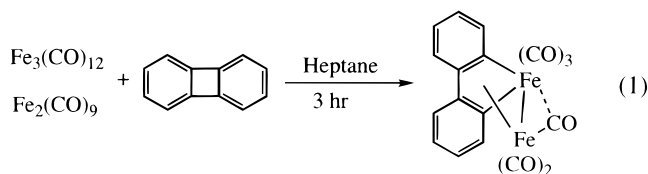
Results and Discussion

Syntheses. Treatment of biphenylene with Fe₃(CO)₁₂ in refluxing heptane (98 °C) for 3 h and subsequent workup by TLC produces Fe₂(CO)₅(μ-CO)(μ-η²,η⁴-(C₆H₄)₂)¹⁴ (**1**), in which one iron atom has inserted into the central carbon–carbon bond of biphenylene, forming a metallacyclopentadienyl moiety, and the cluster nuclearity has changed from 3 to 2. Biphenylene reacts with Fe₂(CO)₉ also leading to **1** as the major metal-containing product (eq 1).

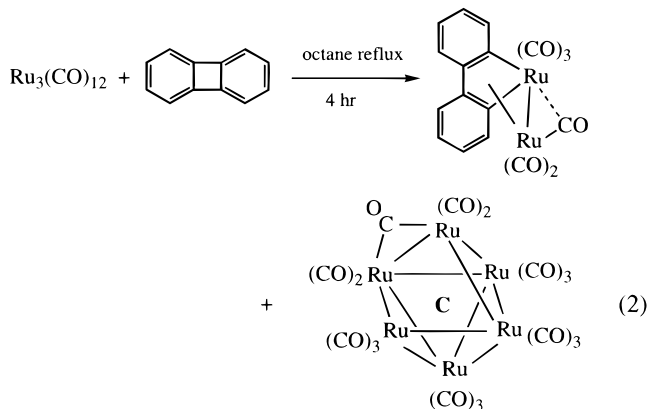
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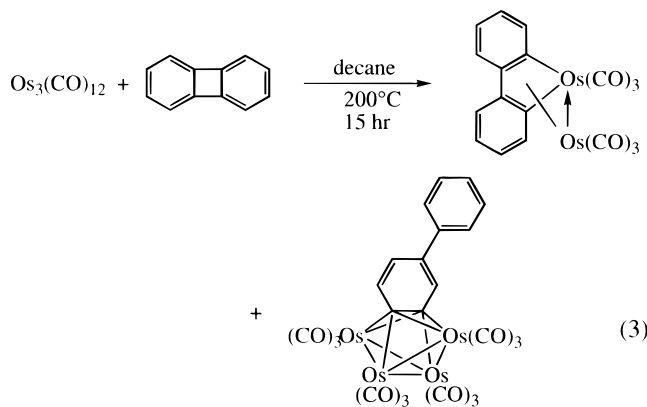


The reaction of biphenylene and $\text{Ru}_3(\text{CO})_{12}$ is carried out in refluxing octane (126 °C), giving $\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (**2**) and the known carbide cluster $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})$ (**3**) (eq 2). Complex **3** was previously



prepared by Lewis and co-workers from thermolysis of $\text{Ru}_3(\text{CO})_{12}$ in hydrocarbon solvents.¹⁵ The source of the carbide carbon in **3** is unknown.

In contrast, the analogous reaction with $\text{Os}_3(\text{CO})_{12}$ requires harsher conditions, in which $\text{Os}_3(\text{CO})_{12}$, biphenylene (5-fold), and 1 mL of decane are mixed in a Teflon-sealed Schlenk tube under N_2 and heated at 200 °C for 15 h, yielding $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (**4**) and $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{Ph)})$ (**5**) (eq 3); a large amount of $\text{Os}_3(\text{CO})_{12}$ (33%) still retains intact. The different reactivity



of iron-triad clusters toward biphenylene is consistent with a stronger M–M and M–CO bond as expected for a third-row transition metal compared with a first-row and a second-row metal.¹⁷

The reaction pathways leading to formation of compounds **1**–**5** are not clear at this stage. Since pure biphenylene is thermally stable to 170 °C, loss of carbonyl ligands from the cluster or breaking a metal–metal bond to generate an unsaturated species seems essen-

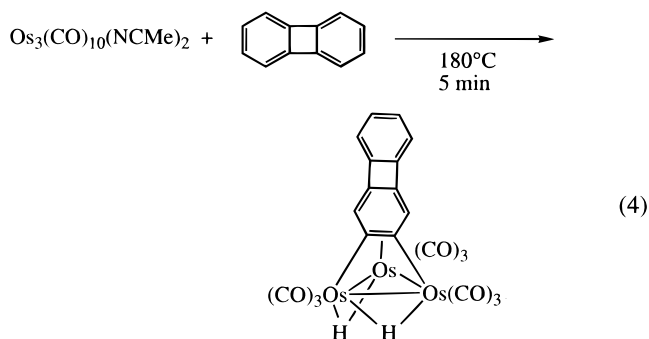
Table 1. Crystallographic Data for $\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (2**), $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (**4**), and $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{Ph)})$ (**5**)**

| | 2 | 4 | 5 |
|---|--|--|---|
| chem formula | $\text{C}_{18}\text{H}_8\text{O}_6\text{Ru}_2$ | $\text{C}_{18}\text{H}_8\text{O}_6\text{Os}_2$ | $\text{C}_{24}\text{H}_8\text{O}_{12}\text{Os}_4$ |
| cryst syst | monoclinic | triclinic | triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| fw | 522.39 | 700.65 | 1249.11 |
| <i>a</i> , Å | 13.227(3) | 8.254(6) | 9.253(4) |
| <i>b</i> , Å | 10.104(3) | 8.767(1) | 10.872(2) |
| <i>c</i> , Å | 13.503(1) | 12.841(3) | 13.534(3) |
| α , deg | 95.298(17) | 85.78(2) | |
| β , deg | 106.51(1) | 102.41(3) | 80.70(3) |
| γ , deg | 104.57(3) | 85.77(3) | |
| <i>V</i> , Å ³ | 1730.3(7) | 867.7(7) | 1337.3(7) |
| <i>Z</i> | 4 | 2 | 2 |
| <i>D</i> _{calc} , g cm ^{−3} | 2.005 | 2.682 | 3.102 |
| μ , cm ^{−1} | 17.430 | 146.759 | 190.255 |
| <i>R</i> ^a | 0.023 | 0.035 | 0.060 |
| <i>R</i> _w ^a | 0.021 | 0.037 | 0.065 |
| GOF | 2.21 | 1.73 | 2.94 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = \{\sum [\omega(|F_o| - |F_c|)^2] / \sum \omega |F_o|^2\}^{1/2}.$$

tial to activate biphenylene, as the 16-electron mononuclear metal fragment is known to cleave arene C–H bonds.¹⁸

It is of interest to compare the reaction of biphenylene with the more labile cluster $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$,¹⁹ while a dihydrido benzyne complex $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_2\text{(C}_6\text{H}_4))$ (**6**) is obtained (eq 4). In this reaction, two



biphenylene C–H bonds, instead of C–C bonds, are activated by the osmium atoms. Nevertheless, this reaction resembles previous observations for the reactions of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with benzene and toluene to give the corresponding benzyne and tolyne complexes.²⁰

Characterization of Products. $\text{Fe}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (**1**) forms air-stable, brownish-red crystals. The ¹H NMR and IR spectra data agree with those previously reported by McWhinnie and co-workers¹⁴ for **1** resulting from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and dibenzotelluraphene $((\text{C}_6\text{H}_4)_2\text{Te})$.

$\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2)$ (**2**) forms air-stable, orange crystals. The FAB mass spectrum shows the molecular ion at *m/z* 524 for ¹⁰²Ru and ions corresponding to successive loss of six carbonyls. The IR spectrum shows a medium absorption at 1882 cm^{−1}, indicating the presence of a bridging carbonyl. The ¹H NMR spectrum (Figure 1) illustrates two doublet and two

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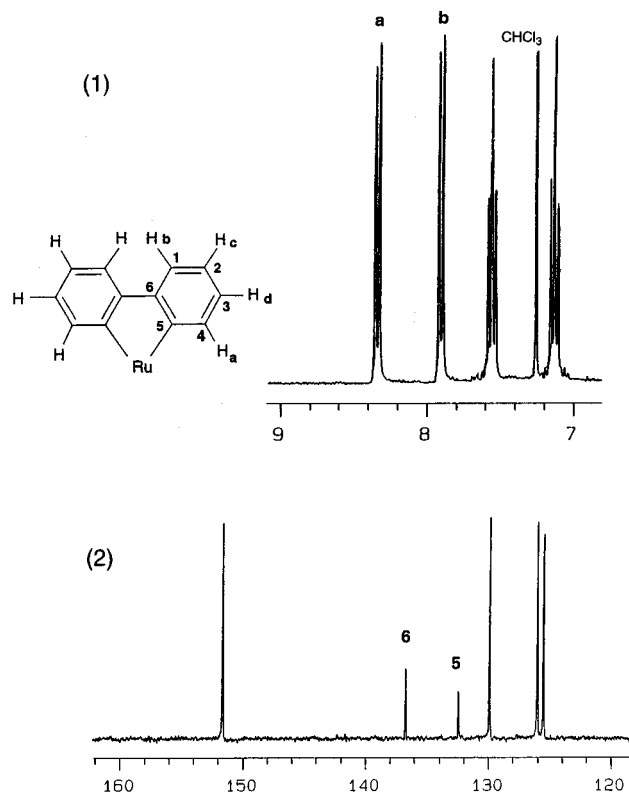


Figure 1. (1) ^1H NMR and (2) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (**2**) obtained in CDCl_3 at 20°C .

triplet signals in the range δ 8.4–7.1 for the phenylene protons. The downfield doublet signal at δ 8.34 can be assigned to the protons ortho to the Ru–C bond, which are expected to be deshielded relative to the other protons.²¹ The $^{13}\text{C}\{^1\text{H}\}$ spectrum is also shown in Figure 1. There are six resonance signals for the 12 biphenylene carbons ranging from δ 151.6 to 125.5, implying a time-averaged C_s symmetry for the molecule. The carbonyl ligands are fluxional at 20°C , as indicated by observing only one broad carbon resonance at δ 188.9.

$\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (**4**) forms air-stable, yellow crystals. The IR absorptions for the carbonyl groups are observed between 2084 and 1974 cm^{-1} with no indication of bridging carbonyl. To determine if different metal sizes and the presence/absence of a bridging carbonyl would affect the binding of the biphenylene ligand, single-crystal X-ray diffraction studies of **2** and **4** were performed.

$\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{)Ph})$ (**5**) forms air-stable, orange-red crystals. The EI mass spectrum shows the molecular ion peak at $m/z = 1256$ for ^{192}Os and ion multiplets corresponding to successive loss of 12 carbonyls. The isotopic distribution of the envelope surrounding the molecular ion matches that expected for **5**, and there is a good agreement between the calculated mass distribution and the observed mass spectrum. The IR absorptions in the carbonyl region show a pattern similar to those recorded for alkyne butterfly clusters $\text{Os}_4(\text{CO})_{12}\text{-(}\mu_4\text{-}\eta^2\text{-alkyne)}$.²² The ^1H NMR spectrum includes a multiplet in the range δ 7.8–7.0 (5H), characteristic of phenyl proton resonances, a singlet at δ 7.13 (1H), a

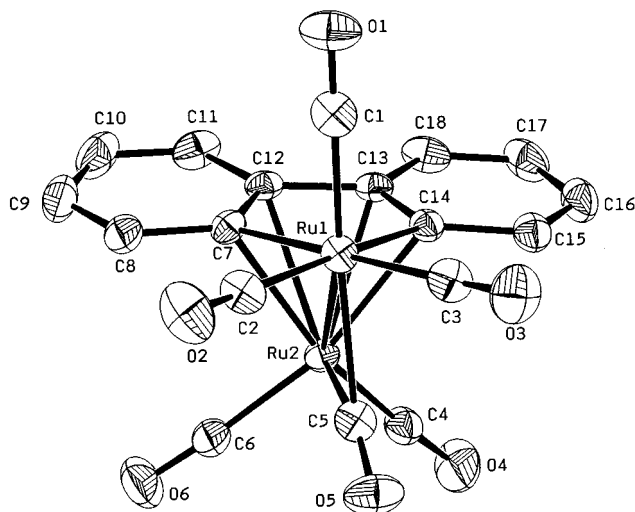


Figure 2. Molecular structure of $\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (**2**). The hydrogen atoms have been artificially omitted for clarity.

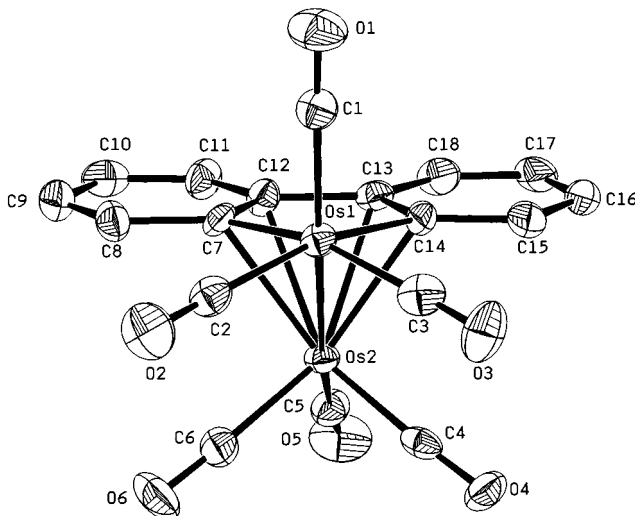


Figure 3. Molecular structure of $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (**4**). The hydrogen atoms have been artificially omitted for clarity.

doublet at δ 6.50 (1H), and a doublet at δ 6.32 (1H). Apparently, the biphenylene molecule has changed its appearance to a different type of ligand. A single-crystal X-ray diffraction study of **5** was thus performed.

$(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_2(\text{C}_6\text{H}_4))$ (**6**) forms air-stable, yellow solids. The IR spectrum in the carbonyl region greatly resembles those recorded for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_4)$ ^{20a} and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_3\text{CH}_3)$.^{20b} The ^1H NMR spectrum includes a singlet at δ –18.99 for the bridging hydrides, a singlet at δ 7.02 for the benzyne ring protons, and a multiplet in the range δ 7.04–6.94 assigned to the protons on the unactivated phenylene ring.

Crystal Structure of 2. Crystals of $\text{Ru}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (**2**) contain an ordered array of discrete monomeric molecule units which are mutually separated by normal van der Waals distances. The ORTEP

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(22) (a) Jackson, R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1980**, 193, C1. (b) Chen, H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1990**, 373.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $\text{Ru}_2(\text{CO})_5(\mu\text{-Co})(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (2) and $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2,\eta^4\text{-(C}_6\text{H}_4)_2)$ (4)

| 2 (M = Ru) | | 4 (M = Os) | | 2 (M = Ru) | 4 (M = Os) |
|------------|------------|------------|-------------|------------|------------|
| Distances | | | | | |
| M1–M2 | 2.6998(6) | 2.7247(11) | C7–C8 | 1.418(7) | 1.425(18) |
| M1–C1 | 1.910(5) | 1.897(15) | C7–C12 | 1.432(6) | 1.463(16) |
| M1–C2 | 1.938(5) | 1.937(14) | C8–C9 | 1.350(8) | 1.353(21) |
| M1–C3 | 1.920(6) | 1.921(17) | C9–C10 | 1.390(9) | 1.432(20) |
| M1–C5 | 2.327(5) | | C10–C11 | 1.346(9) | 1.311(22) |
| M2–C4 | 1.859(5) | 1.866(16) | C11–C12 | 1.415(7) | 1.423(18) |
| M2–C5 | 1.934(5) | 1.933(13) | C12–C13 | 1.474(7) | 1.485(18) |
| M2–C6 | 1.886(5) | 1.890(14) | C13–C14 | 1.425(6) | 1.459(18) |
| M1–C7 | 2.137(4) | 2.087(12) | C13–C18 | 1.419(6) | 1.439(16) |
| M1–C14 | 2.125(4) | 2.124(11) | C14–C15 | 1.421(7) | 1.406(19) |
| M2–C7 | 2.270(4) | 2.366(12) | C15–C16 | 1.360(7) | 1.357(20) |
| M2–C12 | 2.423(4) | 2.357(13) | C16–C17 | 1.389(9) | 1.42(3) |
| M2–C13 | 2.410(4) | 2.356(12) | C17–C18 | 1.344(8) | 1.305(23) |
| M2–C14 | 2.311(4) | 2.366(12) | | | |
| Angles | | | | | |
| M2–M1–C1 | 132.77(14) | 149.4(4) | C4–M2–C7 | 158.60(18) | 140.2(5) |
| M2–M1–C2 | 114.43(14) | 104.1(4) | C4–M2–C12 | 123.27(18) | 151.4(5) |
| M2–M1–C3 | 120.10(15) | 104.9(4) | C4–M2–C13 | 98.89(17) | 115.8(5) |
| M2–M1–C5 | 44.49(12) | | C4–M2–C14 | 100.46(18) | 88.3(5) |
| M2–M1–C7 | 54.48(10) | 57.1(3) | C5–M2–C6 | 96.27(21) | 96.9(6) |
| M2–M1–C14 | 55.73(11) | 56.8(3) | C5–M2–C7 | 98.64(18) | 123.1(5) |
| C1–M1–C2 | 94.20(20) | 96.6(6) | C5–M2–C12 | 129.50(17) | 93.1(5) |
| C1–M1–C3 | 93.91(22) | 96.0(6) | C5–M2–C13 | 122.89(18) | 91.7(5) |
| C1–M1–C5 | 175.51(18) | | C5–M2–C14 | 88.61(18) | 119.0(5) |
| C1–M1–C7 | 88.33(19) | 101.2(6) | C6–M2–C7 | 94.89(18) | 89.0(5) |
| C1–M1–C14 | 91.72(17) | 101.0(5) | C6–M2–C12 | 104.87(18) | 114.1(5) |
| C2–M1–C3 | 92.02(22) | 93.2(6) | C6–M2–C13 | 135.99(19) | 150.3(5) |
| C2–M1–C5 | 90.29(18) | | C6–M2–C14 | 165.77(18) | 143.9(5) |
| C2–M1–C7 | 94.34(20) | 90.3(5) | C7–M2–C12 | 35.33(15) | 36.1(4) |
| C2–M1–C14 | 169.69(19) | 160.9(5) | C7–M2–C13 | 62.65(15) | 62.8(4) |
| C3–M1–C5 | 85.93(20) | | C7–M2–C14 | 71.11(16) | 69.1(4) |
| C3–M1–C7 | 173.09(19) | 161.9(5) | C12–M2–C13 | 35.52(15) | 36.7(4) |
| C3–M1–C14 | 95.99(20) | 92.1(5) | C12–M2–C14 | 62.25(15) | 63.6(4) |
| C5–M1–C7 | 91.33(17) | | C13–M2–C14 | 35.05(15) | 36.0(4) |
| C5–M1–C14 | 83.84(16) | | M1–C5–M2 | 78.04(18) | |
| C7–M1–C14 | 77.39(17) | 79.2(5) | M1–C5–O5 | 133.2(4) | |
| M1–M2–C4 | 138.30(15) | 92.6(3) | M2–C5–O5 | 148.7(4) | 176.0(13) |
| M1–M2–C5 | 57.47(14) | 164.6(4) | M1–C7–M2 | 75.51(4) | 75.1(4) |
| M1–M2–C6 | 123.24(14) | 95.3(4) | M1–C7–C8 | 127.8(3) | 129.4(9) |
| M1–M2–C7 | 50.02(11) | 47.8(3) | M1–C7–C12 | 115.7(3) | 117.2(9) |
| M1–M2–C12 | 72.70(10) | 73.3(3) | C7–C12–C13 | 113.9(4) | 113.1(10) |
| M1–M2–C13 | 72.50(10) | 73.1(3) | C12–C13–C14 | 115.3(4) | 115.3(9) |
| M1–M2–C14 | 49.43(10) | 48.7(3) | M1–C14–M2 | 74.85(13) | 74.5(4) |
| C4–M2–C5 | 100.81(21) | 96.4(5) | M1–C14–C13 | 115.8(3) | 114.9(8) |
| C4–M2–C6 | 91.77(20) | 91.4(6) | M1–C14–C15 | 127.7(3) | 129.2(9) |

drawing is shown in Figure 3. Selected bond distances and bond angles are collected in Table 2.

The Ru1 atom has inserted into the four-membered ring of biphenylene, forming a metallacycle. On the basis of the angles subtended, the coordination about the Ru1 atom can be described as a capped octahedron with the Ru2 atom in the capping position. On the other hand, the coordination about the Ru2 atom is a three-legged piano stool by considering the (Ru1, C7, C12, C13, C14) unit as a metallacyclopentadienyl ligand to bind the Ru2 atom in an η^5 -fashion. The Ru1–Ru2 length is 2.6998(6) Å, typical of a ruthenium–ruthenium single bond. The Ru1 and Ru2 atom are each linked to three and two terminal carbonyl ligands, respectively, with the Ru–C–O angles in the range 175.5(4)–178.7(4)°. The ruthenium–terminal carbonyl distances range from 1.859(5) to 1.938(5) Å, where the longest Ru1–C2 and Ru1–C3 bond lengths might indicate some trans influence from the opposite C14–Ru1 and C7–Ru1 bonds. The carbonyl C5–O5 bridges the Ru1–Ru2 edge unsymmetrically, such that the Ru1–C5 length (2.327(5) Å) is ca. 0.4 Å longer than that of the Ru2–C5 length (1.934(5) Å), and the Ru–C–O angle is bent toward the

Ru1 atom with Ru1–C5–O5 = 133.2(4)° and Ru2–C5–O5 = 148.7(4)°.

The two phenylene rings (C7~C12 and C13~C18) are each planar to within 0.01 and 0.02 Å, respectively while the metallacyclopentadienyl ring is puckered, as evidenced by the torsional angles: Ru1–C7–C12–C13 = 11.9(2)°, Ru1–C14–C13–C12 = 7.8(2)°, C12–C7–Ru1–C14 = 12.3(2)°, and C14–C13–C12–C7 = 2.7(2)°. The phenylene C–C distances are not equal, ranging from 1.344(8) (C17–C18) to 1.432(6) Å (C7–C12). This may indicate little aromaticity of the phenylene rings, apparently due to complexation with the Ru2 atom. The C12–C13 length (1.474(7) Å) is slightly shorter than that in free biphenylene (1.52 Å) and may imply some inter-ring electron delocalization. The Ru1–C bonds at 2.137(4) Å to C7 and 2.125(4) Å to C14, characteristic of σ -bonds, are shorter than the distances of π interactions associated with the Ru2 atom. The Ru2–C bond distances involving the inner carbon atoms, 2.423(4) (C12), 2.410(4) Å (C13), are significantly longer than those involving the outer atoms, 2.270(4) (C7) and 2.311(4) Å (C14). If the neutral biphenylenyl ligand donates 2e[−] to Ru1 and 4e[−] to Ru2 and the bridging carbonyl

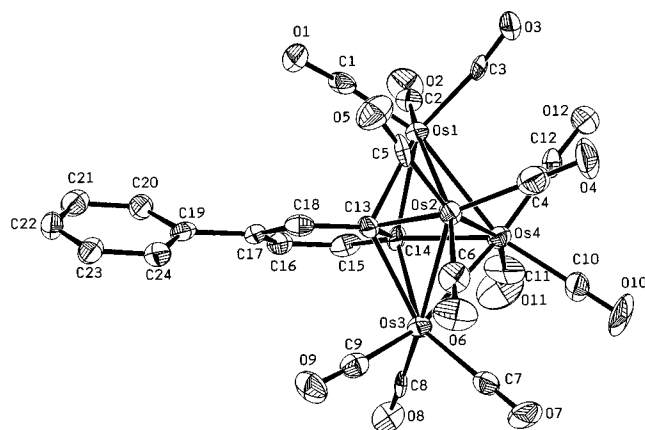


Figure 4. Molecular structure of $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{)-Ph}$) (**5**). The hydrogen atoms have been artificially omitted for clarity.

donates $1e^-$ to each metal, both ruthenium atoms obey the 18-electron rule.

Crystal Structure of 4. The ORTEP drawing of $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^2, \eta^4\text{-(C}_6\text{H}_4)_2$) (**4**) is shown in Figure 3. Selected bond distances and bond angles are given in Table 2. The overall geometry of **4** is very similar to that of **3**, except that no bridging carbonyl is present for **4**. Thus, the coordination about the Os1 atom is a distorted octahedron, and the coordination about the Os2 atom can be described as a three-legged piano stool by considering the metallacycle as an η^5 -ligand. The Os1–Os2 length of 2.725(1) Å is significantly shorter than that observed for the parent compound $\text{Os}_3(\text{CO})_{12}$,²³ in which Os–Os(average) = 2.877(3) Å.

The biphenylenyl group (C7–C18) and the Os1 atom are coplanar to within ± 0.02 Å. The ring carbon–carbon bonds are localized, such that the C8–C9, C10–C11, C15–C16, and C17–C18 bond lengths, ranging from 1.31(2) to 1.36(3) Å, are typical of carbon–carbon double bonds. The C7–C12 and C13–C14 distances are lengthened to 1.46(2) Å, apparently due to π -donation to the Os2 atom. The C12–C13 distance is 1.49(2) Å.

Os1 and Os2 atoms are each linked to three terminal carbonyl ligands. The Os–C–O angles are in the range $176(1)$ – $178(1)^\circ$, and the Os–CO distances range from 1.87(2) to 1.94(1) Å. The Os1 atom forms σ -bonds to C7 and C14 at 2.09(1) and 2.12(1) Å, respectively. The Os2 atom is situated right behind the centroid of the butadiene C7–C12–C13–C14 unit and is about equally bonded to these atoms, with Os–C = 2.36 ± 0.02 Å. Since no bridging carbonyl is present, the Os–Os interaction is best described as a dative bond by donating two nonbonding electrons from Os2 to Os1 to satisfy the 18-electron rule for each osmium atom.

Crystal Structure of 5. An ORTEP diagram of $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{)Ph}$) (**5**) is shown in Figure 4. Selected bond distances and angles are given in Table 3. This complex consists of a tetraosmium butterfly framework bridged by a phenylbenzynes moiety. Complex **5** is the first butterfly cluster of the type $[\text{Os}_4(\text{aryne})\text{-(CO)}_{12}]$, although there are several alkyne complexes of this type.²² The ruthenium analogues $\text{Ru}_4(\mu_4\text{-}\eta^2\text{-naphthyne})\text{(CO)}_{12}$ and $[\text{Ru}_4(\mu_4\text{-}\eta^2\text{-phenanthryne})\text{(CO)}_{12}]$ were recently reported by Deeming and Speel.²⁴

Table 3. Selected Bond Distances and Bond Angles for $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-(C}_6\text{H}_3\text{)Ph}$) (**5**)

| Distances | | | |
|-----------|------------|---------|------------|
| Os1–Os2 | 2.7489(18) | Os1–Os4 | 2.7549(16) |
| Os1–C1 | 1.90(3) | Os1–C2 | 1.95(3) |
| Os1–C3 | 1.908(25) | Os1–C13 | 2.297(22) |
| Os1–C14 | 2.280(21) | Os2–Os3 | 2.7784(14) |
| Os2–Os4 | 2.8830(18) | Os2–C4 | 1.87(3) |
| Os2–C5 | 1.94(3) | Os2–C6 | 1.91(3) |
| C13–C14 | 1.57(4) | Os2–C13 | 2.150(23) |
| C13–C18 | 1.42(4) | Os3–Os4 | 2.7326(17) |
| C14–C15 | 1.43(3) | Os3–C7 | 1.92(3) |
| C15–C16 | 1.37(4) | Os3–C8 | 1.89(3) |
| C16–C17 | 1.41(4) | Os3–C9 | 1.87(3) |
| C17–C18 | 1.37(3) | Os3–C13 | 2.275(22) |
| C17–C19 | 1.48(4) | Os3–C14 | 2.298(23) |
| Os4–C10 | 1.94(3) | Os4–C11 | 1.81(3) |
| Os4–C12 | 1.89(3) | Os4–C14 | 2.101(23) |

| Angles | | | |
|-------------|-----------|-------------|-----------|
| Os2–Os1–Os4 | 63.18(5) | Os1–Os4–C10 | 145.8(10) |
| Os2–Os1–C1 | 107.3(8) | Os1–Os4–C11 | 120.1(11) |
| Os2–Os1–C2 | 159.8(7) | Os1–Os4–C12 | 76.7(7) |
| Os2–Os1–C3 | 91.0(8) | Os1–Os4–C14 | 54.0(6) |
| Os2–Os1–C13 | 49.4(6) | Os2–Os4–Os3 | 59.24(4) |
| Os2–Os1–C14 | 73.3(6) | Os2–Os4–C10 | 96.0(10) |
| Os4–Os1–C1 | 161.2(7) | Os2–Os4–C11 | 160.4(10) |
| Os4–Os1–C2 | 96.8(8) | Os2–Os4–C12 | 103.8(7) |
| Os4–Os1–C3 | 100.8(7) | Os2–Os4–C14 | 72.8(7) |
| Os4–Os1–C13 | 71.9(6) | Os3–Os4–C10 | 91.0(8) |
| Os4–Os1–C14 | 48.2(6) | Os3–Os4–C11 | 102.8(9) |
| C1–Os1–C2 | 91.1(11) | Os3–Os4–C12 | 163.0(7) |
| C1–Os1–C3 | 95.4(11) | Os3–Os4–C14 | 54.9(7) |
| C1–Os1–C13 | 89.5(9) | C10–Os4–C11 | 91.7(16) |
| C1–Os1–C14 | 114.7(9) | C10–Os4–C12 | 89.8(11) |
| C2–Os1–C3 | 95.9(11) | C10–Os4–C14 | 145.3(10) |
| C2–Os1–C13 | 124.3(9) | C11–Os4–C12 | 94.1(11) |
| C2–Os1–C14 | 91.5(9) | C11–Os4–C14 | 90.6(14) |
| C3–Os1–C13 | 139.4(10) | C12–Os4–C14 | 124.5(10) |
| C3–Os1–C14 | 148.9(9) | C13–Os1–C14 | 40.1(9) |
| Os1–Os2–Os3 | 92.58(5) | Os1–Os2–Os4 | 58.51(4) |
| Os1–Os2–C4 | 101.1(10) | Os1–Os2–C5 | 86.2(8) |
| Os1–Os2–C6 | 166.5(9) | Os1–Os2–C13 | 54.3(6) |
| Os3–Os2–Os4 | 57.69(4) | Os3–Os2–C4 | 128.1(10) |
| Os3–Os2–C5 | 135.8(7) | Os3–Os2–C6 | 79.1(8) |
| Os3–Os2–C13 | 53.1(6) | Os1–C13–Os2 | 76.3(7) |
| Os4–Os2–C4 | 87.9(11) | Os1–C13–Os3 | 121.8(10) |
| Os4–Os2–C5 | 144.4(8) | Os1–C13–C14 | 69.4(12) |
| Os4–Os2–C6 | 122.9(9) | Os4–Os2–C13 | 71.2(6) |
| Os2–C13–Os3 | 77.7(8) | C4–Os2–C5 | 95.2(12) |
| Os2–C13–C14 | 107.8(14) | C4–Os2–C6 | 92.4(14) |
| C4–Os2–C13 | 153.4(13) | Os3–C13–C14 | 70.7(11) |
| C5–Os2–C6 | 92.5(12) | C5–Os2–C13 | 92.8(9) |
| C6–Os2–C13 | 112.5(11) | Os1–C14–Os3 | 121.6(10) |
| Os2–Os3–Os4 | 63.08(4) | Os1–C14–Os4 | 77.8(7) |
| Os2–Os3–C7 | 97.7(8) | Os1–C14–C13 | 70.5(11) |
| Os2–Os3–C8 | 160.7(8) | Os2–Os3–C9 | 102.9(7) |
| Os3–C14–Os4 | 76.7(7) | Os2–Os3–C13 | 49.1(6) |
| Os3–C14–C13 | 69.2(12) | Os2–Os3–C14 | 72.5(5) |
| Os4–Os3–C7 | 98.6(8) | Os4–C14–C13 | 108.1(14) |
| Os4–Os3–C8 | 100.4(8) | Os4–Os3–C9 | 163.3(7) |
| Os4–Os3–C13 | 72.6(6) | Os4–Os3–C14 | 48.4(6) |
| C7–Os3–C8 | 94.4(11) | C7–Os3–C9 | 92.1(12) |
| C7–Os3–C13 | 146.4(10) | C7–Os3–C14 | 146.8(10) |
| C8–Os3–C9 | 91.5(11) | C8–Os3–C13 | 118.8(10) |
| C8–Os3–C14 | 89.3(10) | C9–Os3–C13 | 91.4(9) |
| C9–Os3–C14 | 120.8(10) | C13–Os3–C14 | 40.1(9) |
| Os1–Os4–Os2 | 58.31(4) | Os1–Os4–Os3 | 93.45(5) |

Each osmium atom is associated with three terminal carbonyl ligands. The Os–CO distances vary from 1.81–(3) (Os4–C11) to 1.95(3) Å (Os1–C2), while the Os–C–O angles fall in the range $171(3)$ – $173(3)^\circ$. The two hinge $\text{Os}(\text{CO})_3$ groups are staggered, apparently to reduce steric interactions between the CO ligands.

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The benzyne ring carbons are coplanar to within 0.01–(3) Å. The Os–C(benzyne) distances to the hinge Os2 and Os4 atoms, averaging 2.13(2) Å, are significantly shorter than those to the wingtip Os1 and Os3 atoms, averaging 2.29(2) Å. It appears that the benzyne ligand forms σ -bonds with the hinge osmium atoms while it donates its π -electrons to the wingtip osmium atoms. The lengthened C13–C14 bond distance of 1.57(4) Å, typical of a carbon–carbon single bond (i.e., 1.53 Å for ethane), is likely due to back-donation of electrons from the Os atoms into the benzyne π^* orbitals. The remaining benzyne ring carbon–carbon distances show an alternative long–short pattern, implying little aromaticity of this ring. The dihedral angle between the benzyne plane and the phenyl plane is 33(1)°.

Conclusions

The results presented here describe interesting C–C and C–H bond activation of biphenylene by the iron-triad carbonyl clusters. The harsh thermal reaction

conditions also lead to cluster fragmentation with the cluster nuclearity changing from 3 to 2, 4, and 6. Compounds **1**, **2**, and **4** contain a metallacyclopentadienyl group arising from insertion of a metal atom into the central C–C bond of biphenylene. Compound **5** is the first butterfly cluster of the type Os₄(CO)₁₂(aryne), in which the phenylbenzyne ligand is derived from rearrangement of biphenylene molecule. The dihydrido complex **6** comes from C–H bond activation of biphenylene on the triosmium framework.

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Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond angles, bond distances, and torsional angles of **2**, **4**, and **5** (24 pages). Ordering information is given on any current masthead page.

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