

Complexation and C–H bond activation of 1,5-cyclooctadiene on triosmium carbonyl clusters

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Abstract

Reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and 1,5-cyclooctadiene (C_8H_{12}) affords the diene complex $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_8\text{H}_{12})$ (**1**) with the two alkene moieties coordinated to an equatorial and an axial positions of one osmium atom. Thermolysis of **1** in refluxing *n*-hexane results in a vinylic C–H bond activation to form $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu, \eta^4\text{-C}_8\text{H}_{11})$ (**2**) in good isolated yield. The crystal structures of **1** and **2** have been established by an X-ray diffraction study.

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1. Introduction

Triosmium cluster derivatives can be prepared from the parent carbonyl $\text{Os}_3(\text{CO})_{12}$. However, since the Os–CO bond is relatively robust, the substitution reactions are usually carried out at elevated temperature, which often causes ligand decomposition and/or cluster fragmentation [1]. For instance, thermal reaction of $\text{Os}_3(\text{CO})_{12}$ and PPh_3 produces $\text{Os}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1\text{--}3$) and six other products involving P–C and C–H bond activations of the phosphine ligand [2–5], and the reaction of $\text{Os}_3(\text{CO})_{12}$ with biphenylene affords $\text{Os}_2(\text{CO})_6[(\text{C}_6\text{H}_4)_2]$ and $\text{Os}_4(\text{CO})_{12}(\text{C}_6\text{H}_3\text{Ph})$ [6]. Thus, a synthetic strategy by using the unsaturated cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}$ or the “lightly stabilized” complexes $\text{Os}_3(\text{CO})_{12-n}\text{L}_n$ ($\text{L} = \text{nitriles or olefins}$) was developed [7,8]. It turns out that $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ are among the most valuable reagents for the synthesis of a wealth of new triosmium cluster complexes. Shapley and co-workers [9–11], and Lewis and co-workers [12,13] have previously studied

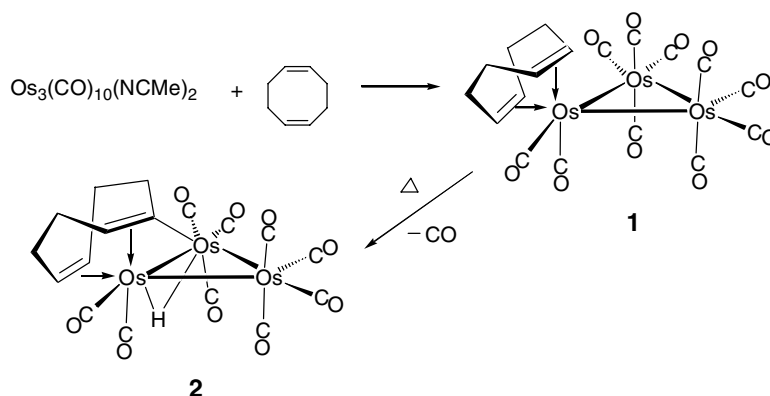
the reactions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with a variety of conjugated dienes. In this paper, we wish to report the synthesis of $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_8\text{H}_{12})$ (**1**), which contains a non-conjugated 1,5-cyclooctadiene ligand, from $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and its reactivity.

2. Results and discussion

The reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and 1,5-COD at room temperature affords **1** in 71% yield after purification by TLC. Previously, the diene complexes $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-cyclohexadiene})$ [13] and $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-norbornadiene})$ [11] were prepared in a same reaction fashion, while $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-butadiene})$ was obtained by treating $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with excess butadiene [9]. Although the isolation of **1** was mentioned [10], no spectroscopic data have been reported. The cyclooctadiene moiety of **1** is labile and can be replaced by PPh_3 to produce the known compound $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ quantitatively at ambient temperature. Compound **1** forms stable yellow solutions in dry organic solvents, whereas the related cyclooctene complex $\text{Os}_3(\text{CO})_{10}(\eta^2\text{-C}_8\text{H}_{14})_2$ decomposes readily in solution [10], and we attribute this difference to the chelate effect. Upon heating, such as in refluxing benzene or *n*-hexane, compound **1** undergoes a vinylic C–H bond activation,

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Scheme 1.

accompanied by a CO loss, to afford the hydrido-dienyl complex $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu, \eta^4\text{-C}_8\text{H}_{11})$ (**2**) in good isolated yield (Scheme 1).

There are two independent but structurally similar molecules in the asymmetric unit for compound **1**, and one of them is depicted in Fig. 1. Selected bond distances and bond angles are collected in Table 1. The compound is characterized by the presence of a 1,5- C_8H_{12} fragment η^4 bonded to a single osmium atom at an equatorial and an axial sites. The three osmium atoms form an isosceles triangle, in which the individual bond lengths are Os2–Os1 2.8755(9) Å, Os2–Os3 2.8772(9) Å, and Os1–Os3 2.9380(9) Å. The Os2 and Os3 atoms are each linked with four carbonyl ligands, while the Os1 atom is linked with two. All carbonyl ligands are terminal and approximately linear. However, the Os–CO bond lengths associated with the Os1 atom (av. 1.86 Å) are significantly shorter than those with the Os2 and Os3 atoms (av. 1.94 Å), indicating a stronger net π back-accepting

Table 1
Selected bond lengths and bond angles for **1**

<i>Bond distances (Å)</i>			
Os1–C16	2.242(2)	Os1–C15	2.264(2)
Os1–C11	2.355(2)	Os1–C12	2.374(2)
Os1–Os2	2.8755(9)	Os1–Os3	2.9380(9)
Os2–Os3	2.8772(9)	C11–C12	1.39(2)
C15–C16	1.37(2)		
<i>Bond angles (°)</i>			
C16–Os1–C15	35.4(6)	C15–Os1–C11	91.0(6)
C15–Os1–C12	75.4(6)	Os2–Os1–Os3	59.32(2)
Os1–Os2–Os3	61.42(2)	Os2–Os3–Os1	59.26(2)
C16–C15–C14	120.9(2)	C15–C16–C17	125.7(1)

capability for the carbonyl ligand compared with olefins [14]. The 1,5-COD is coordinated to Os1 via the atoms C11, C12, C15, and C16, donating four electrons in total, while the equatorial Os1–C15 and Os1–C16 bond distances (av. 2.25 Å) is ca. 0.11 Å shorter than the axial Os1–C11 and Os1–C12 bond distances (av. 2.36 Å). The weaker Os–alkene interactions in the axial position might arise from steric repulsions with the adjacent axial carbonyls. Furthermore, the axial C11–H and C12–H bonds are close to the Os2 and Os3 atoms and should account for the specific vinylic C–H bond activation upon heating to form **2**.

At 25 °C, the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1** depicts a broad signal at 181.6 ppm for the carbonyl carbons, and the ^1H -NMR spectrum displays a 4H siglet at 4.34 ppm for the vinylic protons, and two 4H multiplets at 2.63 and 2.55 ppm for the allylic protons. These data are consistent with a dynamic mechanism, previously established for the fluxional behaviors of $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-cyclohexadiene})$ [15] and $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-norbornadiene})$ [11], which involves complete scrambling of the carbonyls within three osmium atoms and scrambling of the diene ligand around one osmium atom. The proton signals collapse at -50 °C and give rise to 10 broad

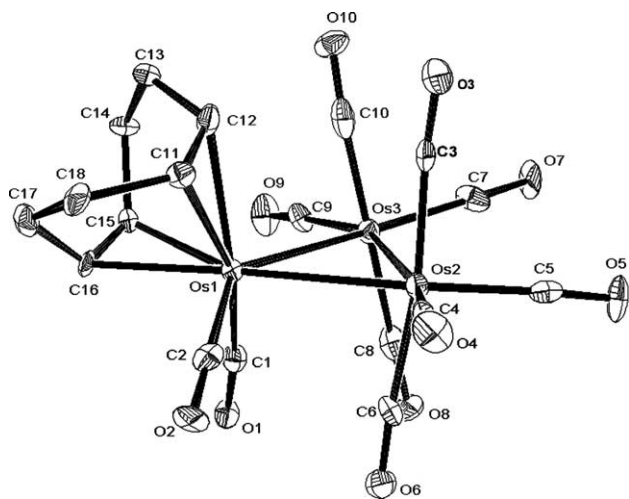


Fig. 1. Molecular structure of **1**. The hydrogen atoms have been artificially omitted for clarity.

peaks between 5.10 and 1.49 ppm at $-105\text{ }^{\circ}\text{C}$ with a ratio of 1:1:1:1:1:1:3:1:1. An idealized slow-exchange spectrum would present 12 distinct proton resonances on the basis of the solid state structure.

The FAB mass spectrum of **2** presents the molecular ion peak at m/z 936 for ^{192}Os . The $^1\text{H-NMR}$ spectrum displays a 1H doublet at 5.31 ppm and two 1H multiplets at 4.43 and 4.20 ppm for the vinylic protons, six multiplets in a 1:1:2:1:2:1 ratio from 3.36 to 1.76 ppm for the allylic protons, and a 1H singlet at -15.75 ppm for the bridging hydride. In order to determine the coordination feature of the dienyl ligand, an X-ray diffraction study was performed. The molecular structure of **2** is shown in Fig. 2, while the selected bond distances and bond angles are collected in Table 2. Compound **2** is based upon a triangular array of osmium atoms in which the Os2–Os3 distance of 2.8680(6) Å is slightly longer than the other intermetallic distances (i.e., an Os1–Os2 distance of 2.8409(6) Å and Os1–Os3 distance of 2.8566(6) Å). The Os1, Os2, and Os3 atoms are each associated with two, three, and four terminal carbonyl groups, respectively, with the Os–C–O angles ranging from $175(1)^{\circ}$ to $178(1)^{\circ}$. The bridging hydride ligand

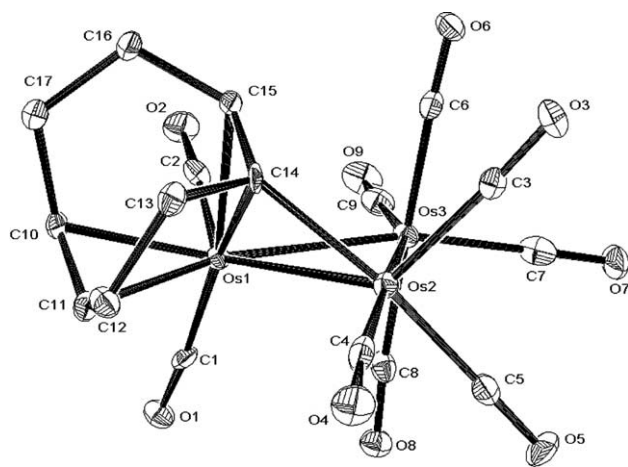


Fig. 2. Molecular structure of **2**. The hydrogen atoms have been artificially omitted for clarity.

Table 2
Selected bond lengths and bond angles for **2**

Bond distances (Å)			
Os1–C11	2.250(1)	Os1–C10	2.257(1)
Os1–C14	2.285(1)	Os1–C15	2.356(1)
Os1–Os2	2.8409(6)	Os1–Os3	2.8566(6)
Os2–Os3	2.8680(6)	Os2–C14	2.166(1)
C10–C11	1.401(2)	C14–C15	1.351(2)
Bond angles ($^{\circ}$)			
C11–Os1–C10	36.2(4)	C14–Os1–C15	33.8(4)
C14–Os1–Os2	48.5(3)	Os2–Os1–Os3	60.447(2)
Os1–Os2–Os3	60.049(2)	Os1–Os3–Os2	59.505(2)
C14–Os2–Os1	52.2(3)	Os2–C14–Os1	79.3(4)

was not located but is believed to span the Os1–Os2 edge. The vinyl carbon C14 bridges the Os1–Os2 edge asymmetrically with the bond lengths C14–Os2 2.17(1) and C14–Os1 2.29(1) Å, and the C15, C10, and C11 atom are bonded to the Os1 atom with the distances C15–Os1 2.36(1) Å, C10–Os1 2.26(1) Å, and C11–Os1 2.25(1) Å. The dihedral angles between the triosmium plane and the Os1–Os2–C14 plane, the Os1–C14–C15 plane, and the Os1–C10–C11 plane are $56.7(4)^{\circ}$, $88.5(7)^{\circ}$, and $38.9(7)^{\circ}$, respectively.

It is interesting that thermolysis of **1** leads to a vinylic C–H bond activation to form the dienyl complex **2**, while heating the cyclohexadiene complex $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)$ in refluxing toluene results in an allylic C–H activation to produce the face-capping compound $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3, \eta^5\text{-C}_6\text{H}_7)$ in low yield [16], and thermolysis of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ in benzene mainly affords the benzyne compound $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_6\text{H}_4)$ [17]. Nevertheless, both allylic and vinylic C–H bond activations of 1,5-COD ligand were recently illustrated in an Ir(I) system [18,19].

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ was prepared by the literature method [20]. 1,5-cyclooctadiene was purchased from Aldrich and distilled before use. 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 CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^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.

3.2. Synthesis of **1**

1,5-Cyclooctadiene (0.8 ml, 76 mmol) was added into a solution of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (50 mg, 0.054 mmol) in CH_2Cl_2 (30 ml). The reaction mixture was stirred at ambient temperature for 4 h. The volatile materials were then removed under vacuum, and the residue was subjected to TLC, eluting with *n*-hexane/ CH_2Cl_2 (5:1, v/v^{-1}). Isolation of the product forming the major yellow band afforded $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_8\text{H}_{12})$ (**1**; 37 mg, 71%). The

single crystals of **1** were grown from *n*-hexane at $-20\text{ }^{\circ}\text{C}$. MS (FAB): m/z 964 (M^+ , ^{192}Os). IR (*n*-hexane, ν_{CO}): 2104m, 2056vs, 2020s, 2000vs, 1984m, 1950vw cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , $25\text{ }^{\circ}\text{C}$): 4.34(s, 4H, =CH), 2.63 (m, 4H, CH_2), 2.55 (m, 4H, CH_2) ppm. $^1\text{H-NMR}$ (CD_2Cl_2 , $-105\text{ }^{\circ}\text{C}$): 5.08 (1H), 4.48 (1H), 3.70 (1H), 3.78 (1H), 3.35 (1H), 3.18 (1H), 2.77 (1H), 2.41 (3H), 1.84 (1H), 1.46 (1H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , $25\text{ }^{\circ}\text{C}$): 181.6 (br, CO), 77.1 (=CH), 33.5 (CH_2) ppm. Anal. found: C, 22.34; H, 1.32. $\text{C}_{18}\text{H}_{12}\text{O}_{10}\text{Os}_3$ Anal. Calc.: C, 22.54; H, 1.26%.

3.3. Thermolysis of **1**

Compound **1** (30 mg) and *n*-hexane (6 ml) were placed in a 25 ml Schlenk flask, equipped with a reflux condenser. The solution was heated to reflux for 20 h under dinitrogen, at which point the IR spectrum showed no absorptions due to the starting cluster. The solvent was removed under vacuum and the residue subjected to TLC, with *n*-hexane/ CH_2Cl_2 (10:3, v/v^{-1}) as eluant. Isolation of the material forming the major yellow band afforded $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu, \eta^4\text{-C}_8\text{H}_{11})$ (**2**; 26 mg, 88%). The single crystals of **2** were grown from CH_2Cl_2 /methanol at $-20\text{ }^{\circ}\text{C}$. MS (FAB): m/z 936 (M^+ , ^{192}Os). IR (*n*-hexane, ν_{CO}): 2096m, 2048s, 2012vs, 1998s, 1982w, 1970m cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , $25\text{ }^{\circ}\text{C}$): 5.31 (d, $J_{\text{H-H}} = 7\text{ Hz}$, 1H), 4.43 (m, 1H), 4.20 (dd, $J_{\text{H-H}} = 3$ and 9 Hz , 1H), 3.35 (d, 1H, $J_{\text{H-H}} = 10\text{ Hz}$), 2.92 (m, 1H), 2.71 (m, 2H), 2.54 (m, 1H), 2.35 (m, 2H), 1.81 (m, 1H), -15.75 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CD_2Cl_2 , $25\text{ }^{\circ}\text{C}$): 188.0, 185.2, 182.5, 181.9, 178.8, 177.3, 175.7, 175.3, 174.9 (CO), 147.2 (HC=C–Os), 106.4 (HC=C–Os), 71.2, 69.9 (HC=CH), 48.4, 43.1, 37.6, 28.7 (CH_2) ppm. Anal. found: C, 21.87; H, 1.44. $\text{C}_{17}\text{H}_{12}\text{O}_9\text{Os}_3$ Anal. Calc.: C, 21.93; H, 1.30%.

4. Structure determination for **1** and **2**

Crystals of **1** and **2** suitable for X-ray diffraction studies were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer with graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The θ range for data collection is $1.60\text{--}27.50^{\circ}$ for **1** and $1.85\text{--}27.50^{\circ}$ for **2**. Of the 22 114 and 15 214 reflections collected for **1** and **2**, 9539 and 4490 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 [21]. A summary of relevant crystallographic data is provided in Table 3.

Table 3
Crystallographic data and refinement details for **1** and **2**

	1	2
Formula	$\text{C}_{18}\text{H}_{12}\text{O}_{10}\text{Os}_3$	$\text{C}_{17}\text{H}_{11}\text{O}_9\text{Os}_3$
<i>T</i> (K)	150	150
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (\AA)	12.6376(2)	8.7620(1)
<i>b</i> (\AA)	12.8994(2)	22.0303(2)
<i>c</i> (\AA)	25.4675(4)	11.0261(1)
β ($^{\circ}$)	–	113.1343(6)
<i>V</i> (\AA^3)	4151.7(1)	1957.21(3)
<i>Z</i>	8	4
<i>D</i> _{calc} (g cm^{-3})	3.068	3.156
μ (mm^{-1})	18.371	19.476
<i>R</i> ₁	0.0471	0.0481
<i>wR</i> ₂	0.0918	0.1277
Goodness-of-fit on <i>F</i> ²	1.026	1.044

5. Supplementary material

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 230240 and 230239, respectively. 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](http://www.ccdc.cam.ac.uk)).

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