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Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Complexation and activation of the bisfulleroid $C_{64}H_4$ with triosmium carbonyl clusters

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ARTICLE INFO

Article history: Received 7 March 2012 Received in revised form 19 May 2012 Accepted 24 May 2012

Keywords:

C–H bond activation of $C_{64}H_4$ C–C activation bond of $C_{64}H_4$ Osmium carbonyl cluster Osmium fullerene complex Cluster fragmentation

ABSTRACT

Reaction of $C_{64}H_4$ (1) and $Os_3(CO)_{10}(NCMe)_2$ in refluxing chlorobenzene affords (μ -H)Os₃(CO)₉(μ , η^4 - $C_{64}H_3$) (2) and $Os(CO)_3(\eta^4$ - $C_{64}H_4)$ (3). Compound 2 apparently arises from C–H bond activation of 1 to generate an η^4 -dienyl motif. In contrast, compound 3 is produced by insertion of one osmium atom into a pentagonal ring of 1, together with the Os₃ cluster fragmentation. Complexes 2 and 3 have been characterized by IR, NMR, and mass spectroscopies. The structure of $3 \cdot C_7H_8$ was determined by a single-crystal X-ray diffraction study.

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1. Introduction

Attachment of organometallic complexes to fullerenes is an important area within fullerene chemistry, due to its potential application in biological, magnetic, electronic, catalytic and optical [1-10]. Meanwhile, preparation endohedral devices of metal-fullerene complexes (with metals inside the fullerene cage) in isolable and stable form remains great challenges [11-14]. Traditional metal/graphite laser and arc evaporation methods are limited in the fullerene size and low product yield [15-20], while an alternative approach by opening a temporary hole within a fullerene framework [21-24], followed by metal complexation and insertion, might provide a promising pathway. Rubin and coworkers have discovered a versatile method leading to the bisfulleroid $C_{64}H_4(1)$ [25], which contains an open cyclooctatriene ring accessible to metal binding. In our continuing interest in metal-fullerene chemistry [26-28], herein we present the complexation and activation reactions of 1 with triosmium carbonyl clusters.

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2. Results and discussion

2.1. Reaction

Reaction of compound **1** and Os₃(CO)₁₀(NCMe)₂ in refluxing chlorobenzene solution leads to the hydrido complex (μ -H) Os₃(CO)₉(μ , η^4 -C₆₄H₃) (**2**; 14%), the mononuclear complex Os(CO)₃(η^4 -C₆₄H₄) (**3**; 37%), and Os₃(CO)₁₂ (25%) after purification by TLC and crystallization (Scheme 1). It appears that compound **2** is obtained from activation of one ethylene C–H bond of **1** by the triosmium cluster to generate a μ -hydrido, η^4 -dienyl bonding motif. On the contrary, compound **3** is produced by insertion of one osmium atom into the pentagon facing the ethylene bridge, together with the Os₃ cluster fragmentation. The complex CpCo(η^4 -C₆₄H₄) analogous to **3** was previously reported by Rubin and coworkers [25] from the reaction of CpCo(CO)₂ and **1**. In contrast, thermal reaction of Os₃(CO)₁₀(NCMe)₂ with the pristine fullerene C₆₀ mainly yielded the face-capping complex Os₃(CO)₉(μ_3 - η^2 , η^2 , η^2 -C₆₀) [29].

2.2. Characterization of 2 and 3

Compound **2** forms an air-stable, green solid. The ESI mass spectrum presents the molecular ion peak at m/z 1600 (¹⁹²Os), corresponding to the combination of **1** with an Os₃(CO)₉ unit. The IR



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Scheme 1. Preparation of 2 and 3.

spectrum in the carbonyl region is shown in Fig. 1, which is similar to that recorded for the hydrido dienyl complex (μ -H) Os₃(CO)₉(μ , η^4 -C₈H₁₁) [30], obtained from thermal reaction of 1,5-cyclooctadiene and Os₃(CO)₁₀(NCMe)₂. The ¹H NMR spectrum of **2** shows two bridging hydride resonances at -15.11 and -15.82 ppm and two sets of hydrocarbon signals in 6.92–5.81 ppm (Fig. 2), indicating the presence of two isomers in an approximate 7:1 ratio. Attempts to separate the two isomers by HPLC or a recrystallization method were not successful. Presumably, the major isomer **2a** contains a 1,2,6,7-dienyl bonding mode, which persists less steric interactions between fullerene and Os₃ cluster, while the minor isomer **2b** can be assigned to the more congested 1,2,4,5-dienyl complex.

Compound **3** forms an air-stable, red solid. The ESI mass spectrum presents the molecular ion peak at m/z 1048 (¹⁹²Os) with the isotope distribution matching the Os(CO)₃(C₆₄H₄) formula. The IR



Fig. 2. 300 MHz 1 H NMR spectrum of 2 in the hydrocarbon region taken in CDCl₃/CS₂ at 23 $^{\circ}$ C, showing the presence of two isomers in a 7:1 ratio.

spectrum displays three terminal carbonyl stretchings at 2091, 2029, and 2017 cm⁻¹. The ¹H NMR spectrum shows the olefinic proton resonances at 7.6 ppm, which is downfield shifted by 0.7 ppm compared to **1** (6.9 ppm) (Fig. 3), consistent with a decrease of electron density on the alkene carbons upon coordination to the osmium atom.

2.3. Structure description of $\mathbf{3} \cdot C_7 H_8$

Crystals of $3 \cdot C_7 H_8$ suitable for an X-ray diffraction study were grown by slow diffusion of *n*-hexane into a CS₂/toluene solution of **3** at ambient temperature. There are two independent but structurally similar complexes in the asymmetric unit, with the ORTEP



Fig. 1. Comparison of the IR spectra of $(\mu$ -H)Os₃(CO)₉ $(\mu, \eta^4$ -C₈H₁₁) and **2** in the carbonyl region; obtained in dichloromethane.

Fig. 3. 300 MHz ¹H NMR spectrum of 1 and 3 taken in CDCl₃/CS₂ at 23 °C.

diagram of one shown in Fig. 4. Compound 3 contains an osmium atom in a distorted octahedral geometry. Remarkably, the C11-C15 edge has been broken by oxidative insertion of the osmium atom with Os1-C11 2.09(1) Å and Os1-C15 2.11(1) Å, and the nonbonding C11…C15 distance is 2.54(5) Å. The ethylene moiety is π -coordinated to the osmium atom with Os1–C4 2.40(1) Å and Os1-C5 2.40(1) Å, which are substantially longer than the Os-C₂(alkene) distances in Os₃(CO)₁₁(η^2 -C₆₀) (av. 2.24 Å) [29], $Os_3(CO)_{10}(\mu, \eta^3 - PPh_2C_{60}H)$ (av. 2.23 Å) [31] and $Os_3(CO)_{10}(\eta^4 - C_8H_{12})$ (av. 2.31 Å) [30], likely due to steric constraints of the bisfulleroid ligand. The three terminal carbonyl ligands occupy the facial position, with the Os–C–O angles ranging from $176(1)-178(1)^{\circ}$. The bond lengths Os1-C1 1.98(1) Å and Os1-C2 1.97(1) Å are 0.1 Å longer than Os1–C3 1.88(1) Å, suggesting a stronger transinfluence from the Os1–C11 and Os1–C15 σ -bond compared to the Os1–C4, 5 π -bond.

2.4. Conclusion

Reactivity of the bisfulleroid molecule **1** towards triosmium carbonyl clusters has been investigated. The ethylene bridge of **1** can undergo a C–H bond activation to give **2**. On the other hand, compound **3** is formed by oxidative insertion of one osmium atom into a five-membered ring of fullerene, leading to an annulene architecture. However, no endohedral Os-fullerene complexes were isolated from the reactions. We are currently exploring the reactions of fullerene derivatives with polynuclear clusters, with an aim to create a large orifice for metal inclusion.

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques.



Fig. 4. Molecular structure of 3 · C7H8 with 30% probability ellipsoids, where the toluene molecule is artificially omitted. Selected bond distances (Å) and bond angles (°): Os1-C1 1.98(1), Os1-C2 1.97(1), Os1-C3 1.88(1), Os1-C4 2.40(1), Os1-C5 2.40(1), Os1-C11 2.09(1), Os1-C15 2.11(1), C4-C5 1.35(2), C4-C9 1.52(2), C5-C6 1.51(2), C6-C7 1.53(2), C6-C16 1.52(1), C7-C8 1.36(2), C8-C9 1.54(2), C9-C10 1.50(2), C10-C11 1.40(2), C11-C12 1.46(2), C12-C13 1.50(2), C13-C14 1.46(2), C14-C15 1.45(1), C15-C16 1.38(2) and Os1-C1-O1 176(1), Os1-C2-O2 176(1), Os1-C3-O3 178(1), Os1-C4-C5 73.8(7), Os1-C4-C9 109.6(7), Os1-C5-C4 73.5(7), Os1-C5-C6 110.1(7), Os1-C11-C10 120.8(8), Os1-C11-C12 121.3(8), Os1-C15-C14 120.5(8), Os1-C15-C16 120.1(8), C1-Os1-C15 172.1(4), C2-Os1-C11 169.8(4), C3-Os1-C4 162.2(5), C3-Os1-C5 163.7(5), C11-Os1-C15 74.7(4), C4-C5-C6 123(1), C4-C9-C8 112(1), C4-C9-C10 113(1), C5-C6-C7 112.5(9), C5-C6-C16 112(1), C6-C7-C8 123(1), C6-C16-C15 119(1), C7-C8-C9 122(1), C8-C9-C10 101.7(8), C9-C10-C11 119(1), C10-C11-C12 116(1), C11-C12-C13 120.4(9), C12-C13-C14 116.8(9), C13-C14-C15 122(1), C14-C15-C16 118(1).

 $Os_3(CO)_{10}(NCMe)_2$ [32] and $C_{64}H_4$ (1) [25] were prepared as described in the literature. 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 on a Jasco FT/IR-4100 IR spectrometer. ¹H and ³¹P NMR spectra were obtained on a Bruker Advance 300 spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Thermo Finnigan Triple Quadrupole mass spectrometer.

3.2. Thermal reaction of Os₃(CO)₁₀(NCMe)₂ and 1

 $Os_3(CO)_{10}(NCMe)_2$ (29 mg, 0.031 mmol), compound **1** (20 mg, 0.026 mmol) and chlorobenzene (10 ml) were placed in an ovendried 50 ml Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. The solution was heated to reflux for 15 min. The solvent was then removed under vacuum, and the residue was subjected to TLC, eluting with CS₂. Isolation of the yellow band afforded $Os_3(CO)_{12}$ (7 mg, 25%), isolation of the green band afforded (μ -H)Os₃(CO)₁₀(μ , η^4 -C₆₄H₃) (**2**; 4 mg, 14%), and isolation of the red band afforded $Os(CO)_3(\eta^4$ -C₆₄H₄) (**3**; 7.1 mg, 37%).

3.2.1. Compound 2

Mass (ESI) *m*/*z*: 1600 (M⁺, ¹⁹²Os). IR (CH₂Cl₂, ν_{CO}): 2100s, 2089w, 2076s, 2048w, 2029s, 2017s, 2004w, 1980w, 1967w cm⁻¹. ¹H NMR (CDCl₃ + CS₂, 23 °C): 6.92 (d, *J*_{H-H} = 6 Hz, 1H), 6.89 (d, *J*_{H-H} = 6 Hz, 0.15H), 6.81 (d, *J*_{H-H} = 2 Hz, 0.15H), 6.26 (dd, *J*_{H-H} = 2 and 6 Hz, 1H), 6.10 (d, *J*_{H-H} = 2 Hz, 1H), 5.81 (dd, *J*_{H-H} = 2 and 6 Hz, 0.15H, C₆₄H₃), -15.11 (s, 1H), -15.82 (s, 0.15H, μ -H) ppm. HRMS (ESI) Calc. for C₇₃H₄N₃O₉Os₃: 1599.8854. Found: 1599.8694.

3.2.2. Compound 3

Mass (ESI) m/z: 1048 (M⁺, ¹⁹²Os). IR (CS₂, ν_{CO}): 2091vs, 2029s, 2017s cm⁻¹. ¹H NMR (CDCl₃+CS₂, 23 °C): 7.63 (m, 2H), 6.66 (m, 2H, C₆₄H₄) ppm. HRMS (ESI) Calc. for C₆₇H₄O₃Os: 1047.9768. Found: 1047.9772.

3.3. Structure determination of $3 \cdot C_7 H_8$

The crystal of $\mathbf{3} \cdot C_7 H_8$ suitable for X-ray analysis was mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.29–25.03°. Of

Formula	C ₇₄ H ₁₂ O ₃ Os
T (K)	200(2)
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	
a (Å)	15.3421(18
b (Å)	16.5423(18
<i>c</i> (Å)	17.847(2)
α (°)	103.299(3)
β(°)	109.647(2)
γ (°)	104.531(4)
$V(Å^3)$	3876.1(8)
Ζ	4
D_{calc} (g cm ⁻³)	1.952
F(000)	2224
$\mu ({\rm mm}^{-1})$	3.360
<i>R</i> ₁	0.0626
$_{W}R_{2}$	0.1427
Goodness-of-fit on F ²	1.086

the 28,175 reflections collected, 13,581 reflections were independent. 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-square cycles. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package. The data collection and refinement parameters are presented in Table 1.

Acknowledgements

This work was financially supported by the National Science Council of Taiwan. We thank Mr. Ting-Shen Kuo (National Taiwan Normal University, Taipei) for X-ray diffraction analysis.

Appendix A. Supplementary material

CCDC 867710 for **3** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac. uk/data_request/cif.

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