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Insertion of bis-ferrocenylbutadiyne into an osmium hydride bond. The synthesis, structure and electrochemical response of $Os_4(CO)_{11}(\mu\text{-}\eta\text{-}Z\text{-}FcCC(H)C_2Fc)(\mu\text{-}H)_3$

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Abstract

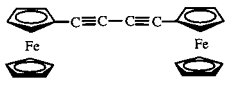
The reaction of $Os_4(CO)_{12}(\mu\text{-}H)_4$ with Me_3NO followed by 1,4-bis(ferrocenyl)butadiyne (**1**) has yielded the tetraosmium product $Os_4(CO)_{11}(\mu\text{-}\eta^2\text{-}FcCC(H)C_2Fc)(\mu\text{-}H)_3$ (**5**), $Fc = C_5H_5FeC_5H_4$ in 9% yield by decarbonylation and insertion of the 1,4-bis(ferrocenyl)butadiyne into one of the metal–hydrogen bonds in the cluster. Compound **5** was characterized by IR, ^{1}H-NMR spectroscopy and single crystal X-ray diffraction analysis. The molecule contains a closed tetrahedral cluster of four osmium atoms with three bridging hydride ligands. One of the C–C triple bonds of **1** was inserted into one of the Os–H bonds to form a (bis-ferrocenyl)yneenyl ligand that bridges one edge of the cluster in a θ-π coordination mode. Compound **5** exhibits two one-electron oxidations for the ferrocenyl groups at $E° = +0.443$ and $+0.486$ V versus Ag/AgCl, $\Delta E° = 0.043$ V. This small difference indicates that there is little or no electronic communication between the two ferrocenyl groups. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; bis-(Ferrocenyl)butadiyne; Insertion; Cluster; Electronic communication

1. Introduction

Bis-(ferrocenyl)butadiyne (**1**) contains two electroactive ferrocenyl groups that can be used to evaluate the electronic communication between the two ends of the molecule [1,2]. Such molecules have attracted attention because the electrochemical response of the electroactive groups can be used as a means to evaluate the potential of the connecting groups to serve as molecular wires for potential use in nanoscale electronic devices [3,4].

We have recently shown that bis-(ferrocenyl)butadiyne can coordinate to osmium cluster complexes in two fundamentally different ways, as shown by the triosmium cluster complexes **2** and **3**, and we have observed that this coordination can significantly effect the electronic communication between the two ferrocenyl groups [5]. In compound **2** the communication is increased relative to that in **1**, $\Delta E = 0.184$ V for **2**, and $\Delta E = 0.100$ V for **1**, but in compound **3** it is decreased, $\Delta E = 0.057$ V. This has been attributed to the influence of the metal atoms on the π-orbital network of the butadiyne grouping.



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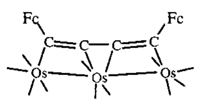

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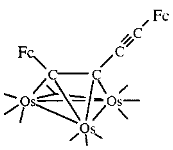

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To try to learn more about the effects of metal atoms on the electronic communication between the ferrocenyl groups in bis-(ferrocenyl)butadiyne metal complexes, we have investigated the reaction of $Os_4(CO)_{12}(\mu\text{-}H)_4$ (**4**) with a combination of trimethylamine-*N*-oxide· dihydrate, $Me_3NO{\cdot}2H_2O$ and **1**. This reaction yielded the new compound $Os_4(CO)_{11}(\mu\text{-}\eta\text{-}Z\text{-}FcCC(H)C_2Fc)(\mu\text{-}H)_3$ (**5**) which was characterized by a combination of single crystal X-ray diffraction analysis and differential pulse voltammetry (DPV). These results are reported here.

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2. Experimental

2.1. General data

Although the reagents and products are air-stable, the reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were freshly distilled prior to use. Trimethylamine *N*-oxide dihydrate was purchased from Sigma-Aldrich and was used without further purification. $Os_4(CO)_{12}(\mu\text{-}H)_4$ was obtained as a side product from the synthesis of $Os_3(CO)_{12}$ [6]. Product separation was performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F_{254} glass plates. Infrared spectra were recorded on a Nicolet 5 DXB FTIR spectrophotometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. DPV measurements were performed by using three-electrode system consisting of a glassy carbon working electrode, a platinum counter and a Ag/AgCl reference electrode on a CV-50 W voltammetric analyzer purchased from Bioanalytical Systems, West Lafayette, IN. Samples were prepared in 1.0 mM solutions by using a $CH_3CN–CH_2Cl_2$ (1:1) solvent mixture containing 0.1 M tetrabutylammonium hexafluorophosphate.

Table 1
Crystallographic data for compound **5**

Formula	$Os_4Fe_2O_{11}C_{35}H_{22}\cdot CH_2Cl_2$
Formula weight	1575.98
Crystal system	Triclinic
Unit cell dimensions	
a (Å)	16.282(2)
b (Å)	16.375(3)
c (Å)	7.946(1)
α (°)	91.79(2)
β (°)	95.22(2)
γ (°)	107.45(2)
V (Å^3)	2009.0(6)
Space group	$P\bar{1}$ (no. 2)
Z	2
D_{calc} (g cm^{-3})	2.60
μ(Mo–K$_\alpha$) (cm^{-1})	134.8
No. of observations, total; $I > 3\sigma(I)$	3756
No. of variables	491
Residuals: ^aR; R_w	0.031; 0.043
Goodness-of-fit (GoF)	1.17
Max shift/final cycle	0.00
Absorption correction (max/min)	DIFABS, 0.42–1.00
Largest residual peak (e Å^{-3})	1.04

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $\text{GoF} = [\Sigma_{hkl}(w(|F_{obs}| - |F_{calc}|))^2/(n_{data} - n_{vari})]^{1/2}$.

2.2. Synthesis of $Os_4(CO)_{11}(\mu\text{-}\eta^2\text{-}Z\text{-}FcCC(H)C_2Fc)(\mu\text{-}H)_3$ (**5**)

A 25.0-mg amount of **4** (0.0227 mmol) was dissolved in 35 ml of CH_2Cl_2 and 10 ml of CH_3CN in a 100-ml three-necked flask at room temperature. A 4.3-mg amount of $(CH_3)_3NO\cdot 2H_2O$ (0.0387 mmol) dissolved in 5 ml of CH_3CN was added dropwise. The color changed immediately from light yellow to a yellow–green. After stirring for 1.5 h, a 10.0-mg amount of **1** (0.0215 mmol) was added into the flask, and the solution was heated to reflux for 30 min. The solvent was then removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was separated by TLC on silica gel with a hexane–CH_2Cl_2 (4:1) solvent mixture. The red product **5** eluted just below the unreacted **1**. Yield 3.0 mg, 9%. IR ν_{CO} (cm^{-1} in hexane): 2098 (s), 2068 (vs), 2054 (vs), 2045 (s), 2023 (m), 2014 (m), 2007 (s), 1997 (m), 1990 (m), 1983 (w), 1978 (w). ^{1}H-NMR (δ in $CDCl_3$): 5.19 (m, 1H, C_5H_4); 4.54 (m, 3H, C_5H_4); 4.53 (m, 2H, C_5H_4); 4.32 (s, 5H, Cp); 4.32 (s, 5H, Cp); 4.30 (m, 2H, C_5H_4); 3.88 (s, 1H, CH); -15.66 (s, 1H, μ-H); -18.75(s, 1H, μ-H); -20.48 (s, 1H, μ-H). Anal. Found: C, 28.19; H, 1.41. Calc.: C, 27.44; H, 1.53.

2.3. Crystallographic analyses

Dark red crystals of **5** were grown by slow evaporation of the solvent from a hexane–CH_2Cl_2 (5:1) solution of the complex at 25°C. A crystal was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation at 20°C. The unit cell was determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The data were processed on a Silicon-Graphics INDIGO2 Workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures [7a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [7b]. Lorentz polarization (L_p) corrections were applied to the data. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F^2_o)/2F_o$ and $\sigma(F^2_o) = [\sigma(I_{raw})^2 + (0.06I_{net})^2]^{1/2}/L_p$.

Compound **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All the structures were solved by a combination of direct methods (SIR-92) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the

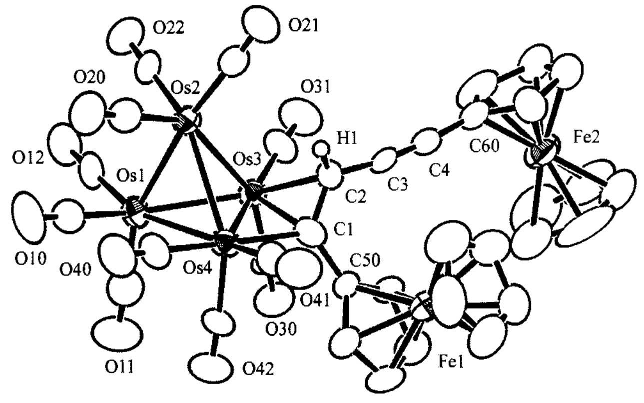


Fig. 1. An ORTEP diagram of $Os_4(CO)_{11}(\mu-\eta-Z-FcCC(H)C_2Fc)(\mu-H)_3$ (**5**) showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (°) are: Os(1)–Os(2) = 2.7920(7), Os(1)–Os(3) = 2.7947(8), Os(1)–Os(4) = 2.9503(7), Os(2)–Os(3) = 2.9547(7), Os(2)–Os(4) = 2.9984(7), Os(3)–Os(4) = 2.7983(6), Os(3)–C(1) = 2.21(1), Os(4)–C(1) = 2.21(1), Os(3)–C(2) = 2.25(1), C(1)–C(2) = 1.41(2), C(2)–C(3) = 1.45(2), C(3)–C(4) = 1.20(2); C(1)–C(2)–C(3) = 125(1), C(2)–C(3)–C(4) = 172(1).

hydrogen atoms on the ferrocenyl groups and H(1) on the C_4 of the ferrocenyl ligand were calculated by assuming idealized tetrahedral geometries at the carbon atoms with C–H distances of 0.95 Å. The scattering contributions of these hydrogen atoms were included in the structure factor calculations, but their positions were not refined. There are three hydride ligands on the cluster of metal atoms. They were not located in the analysis and were ignored.

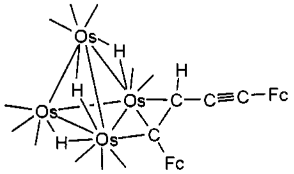
3. Results

The new tetraosmium cluster complex $Os_4(CO)_{11}(\mu$-η-Z-$FcCC(H)C_2Fc)(\mu$-$H)_3$ (**5**), Fc = $C_5H_5FeC_5H_4$ was obtained in 9% yield from the reaction of compound **4** with **1** after pretreatment of the **4** with $Me_3NO{\cdot}2H_2O$.

Compound **5** was characterized by IR and ^{1}H-NMR spectroscopy, single crystal X-ray diffraction analyses and by differential pulse voltammetry. An ORTEP diagram of the molecular structure of compound **5** is shown in Fig. 1. The compound consists of a tetrahedral cluster containing eleven linear terminal carbonyl ligands distributed among the metal atoms as shown in the figure. Most importantly, there is a FcCC(H)C≡CFc ligand that bridges the Os(3)–Os(4) edge of the cluster. The FcCC(H)C≡CFc ligand is coordinated in σ-π bridging coordination mode that is typically observed for alkenyl groups formed by the insertion of alkynes into metal–hydrogen bonds in cluster complexes [8].

The hydrogen atom H(1) on the FcCC(H)C≡CFc was not located directly but was indicated by the presence of a singlet in the ^{1}H-NMR spectrum at $\delta = 3.88$ ppm and the geometry of the ligand. Also, there are three hydride ligands on the cluster. These could not be located directly in the X-ray analysis but their presence was confirmed by the observation of three strongly shielded resonances in the ^{1}H-NMR spectrum at $\delta = -15.66$, -18.75 and -20.48 ppm. Their locations were indicated indirectly by the elongation of the metal–metal bonds that they bridge. Their inferred locations are shown in the line structure below.

The DPV spectrum for **5** shows two poorly resolved one-electron oxidations for the ferrocenyl groups at $E° = +0.443$ and $+0.486$ V, $\Delta E° = 0.043$ V. For comparison, compound **3** also shows two poorly resolved one-electron oxidations centered at $E° = +0.512$ V with the difference between them $\Delta E° \approx 0.057$ V. The free molecule 1,4-bis-ferrocenylbutadiyne also shows two one-electron oxidations for the ferrocenyl groups, but the peak separation is significantly larger, $E_1^\circ = +0.476$ and $E_2^\circ = +0.576$ V with $\Delta E° = 0.100$ V [5].



4. Discussion

The formation of compound **5** is a result of the decarbonylation of **4** induced by the pretreatment with Me_3NO, [9] and the addition and insertion of **1** into one of the Os–H bonds of the cluster. The hydride ligand was shifted to one of the two interior yne carbon atoms of the butadiyne grouping to yield the –C≡C–Fc substituted alkenyl group that bridges an edge of the cluster. The insertion of alkynes into M–H bonds of cluster complexes to yield σ-π coordinated alkenyl groups is well known [8]. However, there are very few examples of the insertion of conjugated diynes into the metal–hydrogen bonds of cluster complexes. Corrigan et al. reported that the reaction of 1,4-diphenylbutadiyne with $Ru_4(CO)_{12}(\mu_3$-$PPh)(\mu$-$H)_2$ yielded the enyne complexes $Ru_4(CO)_{11}[\mu_4$-η^4-$PhC(H)C(H)CCPh](\mu_4$-$PPh)$ and $Ru_4(CO)_{11}[\mu_4$-η^4-$PhC(H)CCC(H)Ph](\mu_4$-$PPh)$ by 1,2 and 1,4-diinsertion of the diyne into the metal–hydrogen bonds of the Ru_4 cluster complex [10].

We have recently reported that the reaction of **3** with water leads to the formation of a partially hydrogenated bis-(ferrocenyl)butadiyne ligand by the addition of a hydrogen atom to one of the two external yne carbon atoms of the butadiyne grouping to yield a μ_3-η^3-FcCCC=C(H)Fc ligand as found in $Os_3(CO)_9(\mu_3$-η^3-Z-$FcC_3CHFc)(\mu$-$OH)$ (**6**) and related compounds [11].

There are a number of examples of the insertion of diynes into the metal–hydrogen bond of mononuclear metal complexes. These insertions proceed by the transfer of the hydride ligand to one of the external alkyne carbon atoms [12,13].

The difference between the oxidation potentials of the ferrrocenyl groups in compound **5** is even smaller than that in compound **3**, and barely larger than that which could be attributed to simple charging effects [1]. Accordingly, it can be surmised that the electronic communication between the ferrocenyl groups in **5** must be very small if there is any at all. One must remember that the ferrocenyl groups in **3** and **5** are intrinsically inequivalent and this also contributes to the difference in the oxidation electrode potentials of these two groupings. It is not possible to separate the combined effects of chemical inequivalence and electronic communication through the carbon chain to determine the relative contribution of each factor to the total. If electronic communication is π-orbital based, then one would expect that the communication in **5** would be small since the only π-orbital between the atoms C(1) and C(2) is involved in bonding to the metal atom Os(3).

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147260 for compound **5**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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