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Butenedithiolate triosmium cluster complexes from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,6-dihydro-1,2-dithiin☆

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Abstract

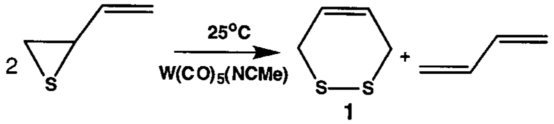
The reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,6-dihydro-1,2-dithiin, $\overline{SCH_2CH{=}CHCH_2S}$, **1** at 0°C yielded two isomeric products $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2**, and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3**. Both compounds were characterized by a combination of IR, ^{1}H-NMR and single-crystal X-ray diffraction analyses. Both compounds contain open triosmium clusters with bridging 2-butene dithiolato ligands formed by cleavage of the S–S bond in **1** and one of the Os–Os bonds in $Os_3(CO)_{10}(NCMe)_2$. In **2** one S atom bridges one of the Os–Os bonds while the other S atom bridges the open edge of the cluster. In **3** both S atoms bridge the open edge of the cluster. In **2** the butenedithiolato ligand has a folded conformation while in **3** this ligand is planar. Compound **2** is converted to **3** and the disomium compound $Os_2(CO)_6(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **4** when heated, but **3** is not converted to **4** under these conditions. Compound **4** contains a 'saw horse' structural arrangement with an Os–Os single bond. The two metal atoms are bridged by the two sulfur atoms of a folded 2-butenedithiolato ligand. Compounds **2** and **4** both exhibit dynamical NMR activity that is related to fluxionality of the butenedithiolato ligand. UV–vis irradiation of **3** results in the cleavage of the two C–S bonds with elimination of butadiene and formation of the disulfido complexes $Os_3(CO)_9(\mu_3\text{-}S)_2$ and $Os_4(CO)_{12}(\mu_3\text{-}S)_2$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cleavage; Triosmium clusters; Butenedithiolate; Dynamical activity

1. Introduction

Organic dithiolates have been shown to be effective chelating ligands in transition metal complexes [1,2]. As bridging ligands they are able to promote the formation and stabilization of polynuclear metal complexes [2]. It has been observed that organic disulfides can be transformed into dithiolate ligands through the cleavage of the sulfur–sulfur bond by metal cluster complexes[3].

In recent studies, we have found that vinylthiirane can be converted into a 1/1 mixture of 3,6-dihydro-1,2-dithiin, $\overline{SCH_2CH{=}CHCH_2S}$, **1** and butadiene in the presence of the catalyst $W(CO)_5(NCMe)$, Eq. (1) [4].



(1)

We have now found that **1** reacts with the triosmium cluster complex, $Os_3(CO)_{10}(NCMe)_2$ via the cleavage of the S–S bond to form two new osmiumdithiolate cluster complexes $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2**, and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3** that each contain a bridging butenedithiolato ligand. With mild heating, compound **2** was converted to **3** and the new diosmium complex $Os_2(CO)_6(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **4**. Thermolysis and photolysis of **3** results in the cleavage of two C–S bonds with elimination of butadiene and formation of the disulfido complexes $Os_3(CO)_9(\mu_3\text{-}S)_2$ [5] and $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ [6]. The results of this study are reported here.

☆ Dedicated to Alan Cowley on the occasion of his 65th birthday.

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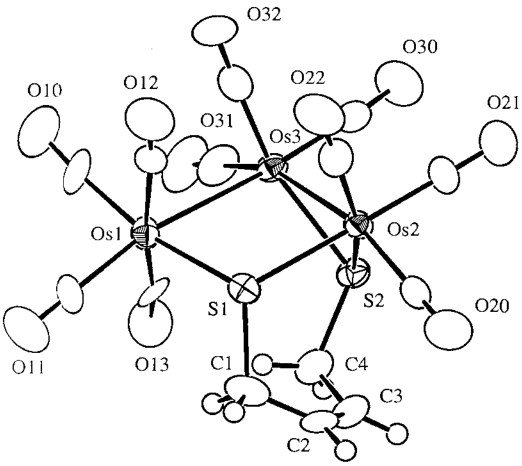


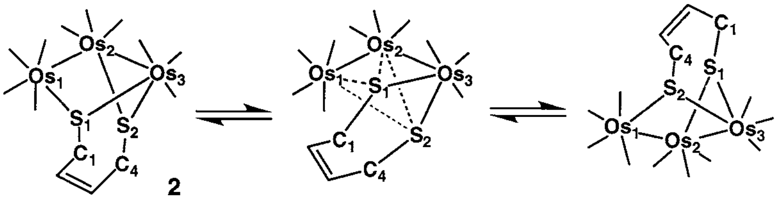
Fig. 1. An ORTEP diagram of $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2** showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Os(1)–Os(2) = 3.921(1), Os(1)–Os(3) = 2.9425(9), Os(2)–Os(3) = 2.821(1), Os(1)–S(1) = 2.440(4), Os(2)–S(1) = 2.444(4), Os(2)–S(2) = 2.404(4), Os(3)–S(2) = 2.431(4), S(1)–C(1) = 1.88(2), S(2)–C(4) = 1.85(2), C(1)–C(2) = 1.48(2), C(2)–C(3) = 1.31(2), C(3)–C(4) = 1.50(2); Os(1)–Os(2)–Os(3) = 85.71(2), Os(1)–S(1)–Os(2) = 106.8(1), Os(2)–S(2)–Os(3) = 71.4(1), S(1)–C(1)–C(2) = 116(1), S(2)–C(4)–C(3) = 109(1), C(1)–C(2)–C(3) = 124(1), C(2)–C(3)–C(4) = 122(1).

2. Results

Two isomeric products, $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2**, and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3**, were obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with **1** at 0°C. Both compounds were characterized by a combination of IR, ^{1}H-NMR and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **2** is shown in Fig. 1. The molecule consists of an open triangular cluster of three osmium atoms. There are bonds between Os(1) and Os(3), and Os(2) and Os(3): Os(1)–Os(3) = 2.9425(9) Å, Os(2)–Os(3) = 2.821(1) Å, but there is no metal–metal bond between the metal atoms Os(1) and Os(2), Os(1)···Os(2) = 3.921(1) Å. A 2-butenedithiolato ligand bridges the three metal atoms with each sulfur atom bridging two osmium atoms. S(1) bridges the non-bonded pair of metal atoms Os(1) and Os(2) and S(2) bridges the bonded pair Os(2) and Os(3). The Os(2)–Os(3) bond is significantly shorter than the Os(1)–Os(3) bond. This shortening can probably be attributed to a contraction effect produced by the bridging sulfur atom S(2). There is a double bond between the carbon atoms C(2) and C(3), C(2)–C(3) = 1.31(2) Å. The structure of **2** is similar to that of the compound $Os_3(CO)_{10}(\mu\text{-}Sdmpymt)_2$, **5**, dmpymt = 4,6-dimethylpyrimidin-2-yl having two bridging Sdmpymt ligands that was recently obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with the disulfide, dmpymtS–Sdmpymt [7]. Two structurally related bis-selenate containing clusters $Os_3(CO)_{10}(\mu\text{-}SePh)_2$ and $Os_3(CO)_{10}(\mu\text{-}SeMe)_2$ obtained from the reactions of $Os_3(CO)_{11}(NCMe)$ with the corresponding diselenides have been reported recently [8].

Interestingly, the ^{1}H-NMR spectrum of **2** at room temperature shows six broad featureless singlets at δ = 5.63, 4.95, 3.18, 2.44, 2.07, and 1.71 ppm. Dynamical activity was suspected and subsequently confirmed by variable temperature ^{1}H-NMR measurements. At −40°C the spectrum exhibits six sharp well resolved multiplets: δ = 5.48 ddd, 4.79 ddd, 3.00 dd, 2.23 dd, 1.72 dd, 1.28 dd with coupling constants consistent with the structure found in the solid state. At temperatures above 25°C, the resonances broaden further and merge into three pairs at approximately 50°C. Spectra at higher temperatures are complicated because of a simultaneous conversion of **2** to **3** and **4** whose resonances overlap those of **2**. The higher temperature limiting spectrum was not obtained. Nevertheless, it was possible to calculate a free energy of activation for the rearrangement at the coalescence temperature, $\Delta G^{\neq}_{323} = 14.8(3)$ kcal mol^{-1}. The spectral changes indicate that the inequivalent protons on the methylene group C(1) are averaged pair-wise with the inequivalent protons on C(4) and the olefinic proton on C(2) is averaged with the proton on C(3). A mechanism that can account for the spectral changes is shown in Scheme 1. By this mechanism the sulfur atoms interchange their positions. Os-S bonds are broken between the atoms Os(1) and S(1) and Os(2) and S(2) and similar bonds are formed between Os(2) and S(1) and Os(1) and S(2). As a consequence the protons on C(1) are interchanged pair-wise with those on C(4) and the proton on C(2) is interchanged with the one on C(3). Compound **3** is not an intermediate in this process.

The crystal of **3** contains two independent molecules. Both molecules are structurally similar. An ORTEP



Scheme 1.

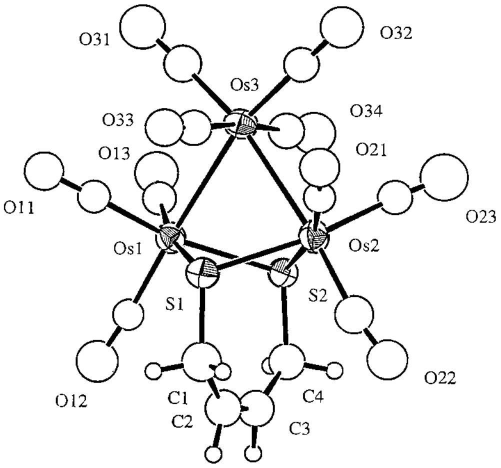


Fig. 2. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3** showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Os(1)–Os(2) = 3.396(1), Os(1)–Os(3) = 2.898(2), Os(2)–Os(3) = 2.907(2), Os(1)–S(1) = 2.425(9), Os(1)–S(2) = 2.436(8), Os(2)–S(1) = 2.425(9), Os(2)–S(2) = 2.44(1), S(1)–C(1) = 1.82(4), S(2)–C(4) = 1.83(4), C(1)–C(2) = 1.47(5), C(2)–C(3) = 1.27(5), C(3)–C(4) = 1.49(5), Os(4)–Os(5) = 3.396(1), Os(4)–Os(6) = 2.903(2), Os(5)–Os(6) = 2.904(2), Os(4)–S(3) = 2.42(1), Os(4)–S(4) = 2.428(9), Os(5)–S(3) = 2.422(8), Os(5)–S(4) = 2.430(9), S(3)–C(5) = 1.80(4), S(4)–C(6) = 1.83(4), C(5)–C(6) = 1.46(5), C(6)–C(7) = 1.36(5), C(7)–C(8) = 1.43(5); Os(1)–Os(3)–Os(2) = 71.62(5), Os(1)–S(1)–Os(2) = 88.9(3), Os(1)–S(2)–Os(1) = 88.2(1), S(1)–C(1)–C(2) = 126(3), S(2)–C(4)–C(3) = 123(3), C(1)–C(2)–C(3) = 139(4), C(2)–C(3)–C(4) = 139(4), Os(4)–Os(6)–Os(5) = 71.59(5), Os(4)–S(3)–Os(5) = 89.1(3), Os(4)–S(4)–Os(5) = 88.7(3), S(3)–C(5)–C(6) = 127(3), S(4)–C(8)–C(7) = 126(3), C(5)–C(6)–C(7) = 133(4), C(6)–C(7)–C(8) = 141(4).

drawing of one of these molecules is shown in Fig. 2. This molecule also consists of an open triangular cluster of three osmium atoms: Os(1)···Os(2) = 3.396(1) Å [Os(4)···Os(5) = 3.396(1) Å] Os(1)–Os(3) = 2.898(2) Å [Os(4)–Os(6) = 2.903(2) Å], Os(2)–Os(3) = 2.907(2) Å [Os(5)–Os(6) = 2.904(2) Å], values in brackets correspond to the second molecule in the crystal. There is no bond between atoms Os(1) and Os(2) [Os(4) and Os(5)]. Compound **3** also contains a 2-butenedithiolato ligand, but in this molecule both sulfur atoms bridge the two nonbonded osmium atoms. There is a double bond between the carbon atoms C(2) and C(3) [C(6) and C(7)]: C(2)–C(3) = 1.27(5) [C(6)–C(7) = 1.36(5)]. The structure of **3** is similar to that of the compound $Os_3(CO)_{10}(\mu\text{-}Sdmpymt)_2$ which was obtained by thermal isomerization of **5**, [7] and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$ which was obtained by the elimination of ethylene from the complex $Os_3(CO)_{10}(SCH_2CHSCHCH_2)$ [9]. Curiously, in this molecule the 2-butenedithiolato ligand is planar and quite unlike the folded form found in the structure of **2**. Based on the large bond angles with the ligand: S(1)–C(1)–C(2) = 126(3) [S(3)–C(5)–C(6) = 127(3)], S(2)–C(4)–C(3) = 123(3) [S(4)–C(8)–C(7) = 126(3)], C(1)–C(2)–C(3) = 139(4) [C(5)–C(6)–C(7) = 133(4)] C(2)–C(3)–C(4) = 139(4) [C(6)–C(7)–C(8) = 141(4)], particularly the C–C–C angles which lie in the region of 140°, one would suspect that the ligand is in a state of minor strain, but there is evidently no simple mechanism for relieving this. Folding of the ligand appears to be prevented by steric interactions with the carbonyl ligands C(12)–O(12) and C(22)–O(22).

A second compound is also formed when compound **2** is heated. This compound has been identifed as $Os_2(CO)_6(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **4** and is obtained in 34% yield. Compound **4** was also characterized crystallographically. An ORTEP diagram of the molecular structure of **4** is shown in Fig. 3. Compound **4** contains two $Os(CO)_3$ groups in the 'saw horse' structural arrangement with an Os–Os single bond, Os(1)–Os(2) = 2.724(1) Å. The two metal atoms are bridged by the two sulfur atoms of a 2-butenedithiolato ligand. In this molecule, the butenedithiolato ligand is folded in a manner similar to that found in **2**. The methylene proton resonances appear as a single well-resolved multiplet 3.13 ppm (4H) and the alkenyl protons appear as a well resolved multiplet 5.94 ppm (2H) at 25°C. Interestingly, the ^{13}C spectrum of **4** showed only two ^{13}C CO resonances at 176.64 ppm 172.07 ppm in a 2/1 ratio. Low-temperature ^1H-NMR spectra confirmed the existence of a dynamical process. At − 65°C the spectrum shows two broad singlets for the inequivalent CH_2 protons at 3.44 (2H) and 2.77 (2H) ppm, as expected on the basis of the structural analysis. As the temperature is raised, the resonances broaden and merge, coalescing at − 50°C [$\Delta G^{\neq}_{223} = 10.1(2)$ kcal mol^{-1}] and then re-

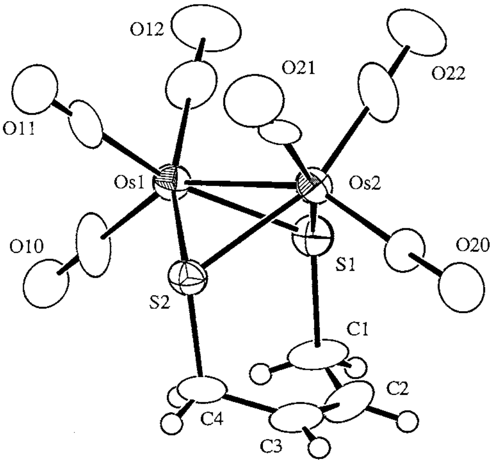
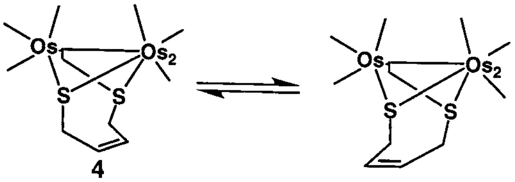


Fig. 3. An ORTEP diagram of $Os_2(CO)_6(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **4** showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Os(1)–Os(2) = 2.724(1), Os(1)–S(1) = 2.421(5), Os(2)–S(1) = 2.410(5), Os(2)–S(1) = 2.420(5), Os(2)–S(2) = 2.416(4), S(1)–C(1) = 1.87(2), S(2)–C(4) = 1.85(2), C(1)–C(2) = 1.44(3), C(2)–C(3) = 1.31(3), C(3)–C(4) = 1.52(3); Os(1)–S(1)–Os(2) = 68.5(1), Os(1)–S(2)–Os(2) = 68.7(1), S(1)–C(1)–C(2) = 118(2), S(2)–C(4)–C(3) = 114(1), C(1)–C(2)–C(3) = 121(2), C(2)–C(3)–C(4) = 122(2).

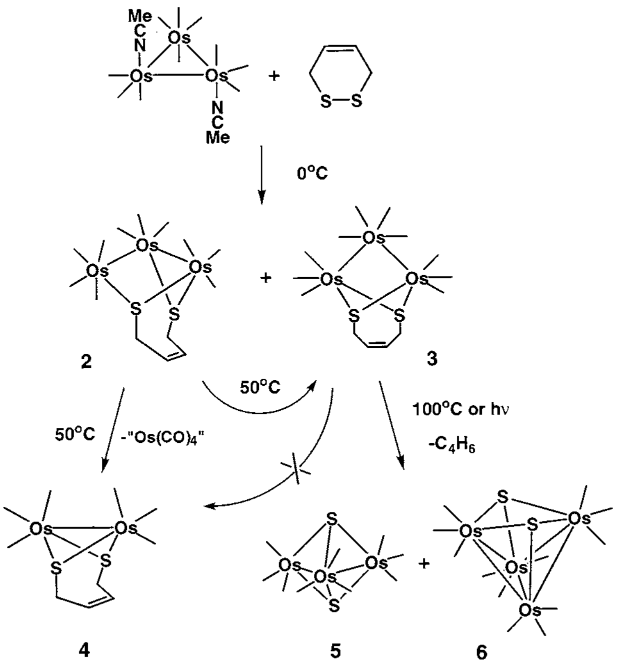


Scheme 2.

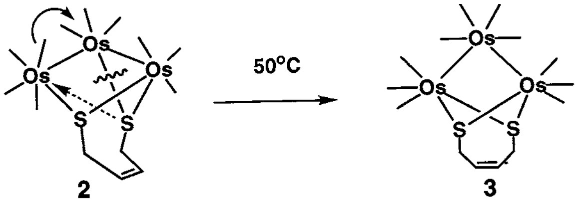
forming as a single multiplet at 25°C. We have interpreted these observations in terms of a dynamical process involving an inversion in the configuration of the fold of the butenedithiolato ligand as shown in Scheme 2. This process leads to a pair-wise averaging of the inequivalent methylene protons and the carbonyl groups on the different metal atoms. We were unable to convert **3** to **4**, but under UV–vis irradiation the two known disulfude cluster complexes $Os_3(CO)_9(\mu_3\text{-}S)_2$ [5] (56% yield) and $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ [6] (5% yield) were formed by elimination of butadiene. The same products are produced thermally at 100°C but the yields are much lower.

3. Discussion

A summary of the results of this study is given in Scheme 3. Two products, **2** and **3**, are formed from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with **1** at 0°C by a process that leads to elimination of the two NCMe ligands and the interaction of one equivalent of **1** with cleavage of its S–S bond and a cleavage of one Os–Os bond. Compound **2** converts to compound **3** at ambient temperature and it appears that all of the **3** is derived from **2** by this transformation that involves a shift of one CO ligand between two metal atoms and a shift of the thiolato sulfur that bridges the Os–Os bond to a bridging position between the nonbonded pair of metal atoms, see Scheme 4. Interestingly, the observation that **2** forms before **3** provides information about the mechanism of the cluster opening process. That is, the formation of **2** must occur by cleavage of one of the Os–Os bonds of the $Os(CO)_4$ group and not the Os–Os bond located between the two $Os(CO)_3NCMe$ groups in $Os_3(CO)_{10}(NCMe)_2$. In a competing process, **2** also expels an $Os(CO)_4$ group to form **4**. Interestingly, **3** is not converted to **4** under these conditions, indicating that loss of $Os(CO)_4$ from **3** is considerably more difficult than from **2**. This may be related to the fact that loss of $Os(CO)_4$ from **3** requires the cleavage of two Os–Os bonds while loss of $Os(CO)_4$ from **2** requires the cleavage of only one Os–Os bond. Under more forcing conditions, **3** was observed to eliminate butadiene to yield the known compound **5** together with small amounts of the tetraosmium compound **6**.



Scheme 3.



Scheme 4.

4. Experimental

4.1. General data

Reagent grade solvents were freshly distilled and stored over 4 Å molecular sieves. All reactions were performed under a nitrogen atmosphere unless otherwise specified. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^1H-NMR spectra were recorded on Varian Mercury spectrometers at 400 or 500 MHz. ^{13}C-NMR spectra were recorded on a Varian Mercury spectrometer at 100.60 MHz. $Os_3(CO)_{10}(NCMe)_2$ [10] and 3,6-dihydro-1,2-dithiin [4] **1** were prepared according to the published procedures. Product separations were performed by TLC in air on Analtech 0.25 and 0.50 mm silica gel 60 Å F_{254} glass plates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

4.2. Reaction of $Os_3(CO)_{10}(NCMe)_2$ and 3,6-dihydro-1,2-dithiin, **1**

A total of 100.0 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.107 mmol) was dissolved in 30 ml of methylene chloride at 0°C in a 50 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. A 1.5 equivalent (0.161 mmol) of **1** was added and the solution was stirred for 30 min. The volatiles were removed in vacuo, and the product was isolated by TLC using a hexane/methylene chloride 4/1 solvent mixture to yield 29.9 mg (28%) of $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2**, and 24.6 mg (23%) of $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3**. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2111 (m), 2069 (vs), 2047 (s), 2036 (vs), 2017 (m), 2006 (m), 1995 (s), 1984 (m), 1969 (w), 1961 (w). ^{1}H-NMR (δ in toluene-d_8, 25°C): $\delta = 5.63$, 4.95, 3.18, 2.44, 2.07, 1.71 ppm. ^{1}H-NMR (δ in toluene-d_8, -40°C, Hz): 5.48 (ddd, $^3J_{H\text{-}H} = 6.3$, $^3J_{H\text{-}H} = 11.0$, $^3J_{H\text{-}H} = 8.8$, 1H), 4.79 (ddd, $^3J_{H\text{-}H} = 8.0$, $^3J_{H\text{-}H} = 7.6$, $^3J_{H\text{-}H} = 8.8$, 1H), 3.00 (dd, $^2J_{H\text{-}H} = 11.2$, $^3J_{H\text{-}H} = 6.3$, 1H), 2.23 (dd, $^2J_{H\text{-}H} = 11.2$, $^3J_{H\text{-}H} = 11.0$, 1H), 1.72 (dd, $^2J_{H\text{-}H} = 12.0$, $^3J_{H\text{-}H} = 8.0$, 1H), 1.28 (dd, $^2J_{H\text{-}H} = 12.0$, $^3J_{H\text{-}H} = 7.6$, 1H) $[\Delta G^{\neq}_{323} = 14.8(3)$ kcal mol$^{-1}]$ $C_{14}H_6O_{10}S_2Os_3$: Anal. Calc. C 17.35, H 0.62. Found C 17.56, H 0.66. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2105 (w), 2065 (s), 2054 (w), 2020 (vs), 1989 (m), 1980 (sh). ^{1}H-NMR (δ in toluene-d_8, 25°C, Hz): 5.30 (t, $^3J_{H\text{-}H} = 3.3$, 2H), 3.36 (d, $^3J_{H\text{-}H} = 4.0$, 4H). ^{13}C-NMR (δ in toluene-d_8, 25°C): 179.09 (4C), 177.53 (2C), 175.72 (2C), 169.09 (2C), 129.31 (2C), 44.83 (2C). $C_{14}H_6O_{10}S_2Os_3$: Anal. Calc. C 17.35, H 0.62. Found C 17.86, H 0.32.

4.3. Thermolysis of $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CH{=}CHCH_2S)$, **2**

A 27.5 mg sample of **2** (0.0284 mmol) was dissolved in 1.0 ml toluene-d_8 and placed in an NMR tube. The tube was then heated to 50°C for 4 h. The ^{1}H-NMR spectrum showed all of **2** had been consumed. The volatiles were removed in vacuo and the product was isolated by TLC using hexane eluant to yield 6.5 mg (34%) $Os_2(CO)_6(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **4**, and 2.6 mg (9%) **3**. Spectral data for **4**: IR ν_{CO} (cm^{-1} in hexane): 2086 (m), 2056 (vs), 2003 (vs), 1995 (s), 1984 (m). ^{1}H-NMR (δ in $CDCl_3$, 25°C, Hz): 5.94 (m, 2H), 3.13 (m, 4H); (in $CDCl_3$, -60°C): 5.94 (m, 2H), 3.44 (s, br, 2H), 2.77 (s, br, 2H). ^{13}C-NMR (δ in $CDCl_3$, 25°C): 176.64 (4C), 172.07 (2C), 135.91 (2C), 30.92 (2C). $C_{10}H_6O_6S_2Os_2$: Anal. Calc. C 18.02, H 0.90. Found C 18.25, H 0.84.

4.4. Thermolysis of $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3**

A total of 31.0 mg of **3** (0.0320 mmol) was dissolved in 1.0 ml toluene-d_8 and placed in an NMR tube. The tube was then heated to 100°C for 48 h. An NMR spectrum showed a decrease in starting material and formation of butadiene. The volatiles were removed in vacuo and the products were isolated by TLC using hexane eluant to yield 3.0 mg (11%) $Os_3(CO)_9(\mu_3\text{-}S)_2$, 2.0 mg (5%) $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, and 21.3 mg (69%) unreacted **3**.

4.5. Photolysis of $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CHCH_2S)$, **3**

A 10.0 mg sample of **3** (0.0103 mmol) was dissolved in 1.0 ml toluene-d_8 and placed in an NMR tube. The tube was then irradiated by using a 360 W high-pressure Hg lamp for 60 min. The NMR spectrum showed only solvent peaks and butadiene. The volatiles were removed in vacuo and the products were isolated by TLC using hexane eluant to yield 5.1 mg (56%) $Os_3(CO)_9(\mu_3\text{-}S)_2$, 0.6 mg (5%) $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, and 1.0 mg unreacted **3**.

4.6. Crystallographic analysis

Golden–yellow crystals of **2** and **3** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at -17°C. Yellow crystals of **4** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 25°C. All crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo–K_α radiation at 23°C. The unit cells of the crystals were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. The crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Silicon-Graphics INDIGO^2 Workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure, The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [11a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [11b]. Lorentz/polarization (Lp) corrections were applied to the data for each structure. Full matrix least-squares refinements minimized the function: $\Sigma_{hkl}\, w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/\text{Lp}$.

Compound **2** 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. The structure was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included without refinement in calculated positions.

Table 1
Crystallographic data for compounds **2**, **3** and **4**

Maximum shift/error on final cycle Compound	$Os_3S_2O_{10}C_{14}H_6$ **2**	$Os_3S_2O_{10}C_{14}H_6$ **3**	$Os_2S_2O_6C_{10}H_6$ **4**
Empirical formula	$Os_3S_2O_{10}C_{14}H_6$	$Os_3S_2O_{10}C_{14}H_6$	$Os_2S_2O_6C_{10}H_6$
Formula weight	968.92	968.92	666.67
Crystal system	Triclinic	Orthorhombic	Monoclinic
Lattice parameters			
a (Å)	9.845(2)	13.724(2)	7.854(1)
b (Å)	12.682(2)	32.064(7)	16.443(3)
c (Å)	9.705(2)	9.554(1)	12.256(1)
α (°)	99.79(2)	90	90
β (°)	118.37(1)	90	105.63(1)
γ (°)	76.10(2)	90	90
V (Å^3)	1032.6(4)	4205.3(10)	1524.2(4)
Space group	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)	$P2_1/n$ (#14)
Z	2	8	4
$D_{calc.}$ (g cm^{-3})	3.12	3.06	2.90
μ (Mo–K$_\alpha$) (cm^{-1})	186.51	182.86	169.37
$2\Theta_{max}$ (°)	43	47	43
Observed reflections ($I>3\sigma(I)$)	2023	2890	1476
Number of variables	263	284	181
Goodness-of-fit (GOF)	1.94	2.61	2.49
Maximum shift/error on final cycle	0.00	0.00	0.00
[a]Residuals: R; R_w	0.034; 0.041	0.047; 0.051	0.043; 0.052
Abs. cor.	DIFABS	DIFABS	DIFABS
Max/min transmission	1.00–0.67	1.00–0.38	1.00–0.42
Largest difference peak (e Å^{-3})	1.28	1.55	1.58

[a] $R=\Sigma_{hkl}(\|F_o|-|F_c\|)/\Sigma_{hkl}|F_o|$; $R_w=[\Sigma_{hkl}w(|F_o|-|F_c|^2)/\Sigma_{hkl}wF_o^2]^{1/2}$, $w=1/\sigma^2(F_o)$; $GOF=[\Sigma_{hkl}(w(|F_o|-|F_c|))^2/(n_{data}-n_{vari})]^{1/2}$.

Compound **3** crystallized in the orthorhombic crystal system with two formula equivalents of the molecule in the asymmetric unit. The space group $P2_12_12_1$ was established from the patterns of systematic absences observed during the collection of intensity data. The structure was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. Due to the limited amount of data, only atoms heavier than oxygen were refined with aniotropic thermal parameters. Hydrogen atoms were included without refinement in calculated positions. This refinement produced the residuals $R=0.055$ and $R_w=0.063$. To test for the enantiomorph, all positional coordinates of the atoms were then inverted and the structure was refined again. This second refinement produced the residuals $R=0.047$ and $R_w=0.051$. The significant improvement in the residuals indicates that this is the correct enantiomorph. These values were retained and are the ones reported here.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established from the patterns of systematic absences observed during the collection of intensity data. The structure was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included without refinement in calculated positions with C–H distances of 0.95 Å.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 112279 for **1**, 112280 for **2** and, 112281 for **3**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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