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The effect of a vinyl substituent on the ring opening of a substituted tetrahydrothiophene at a triosmium center

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Abstract

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-vinyltetrahydrothiophene (VTHT) at 25°C yielded two products: $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2C(H){=}C(H)C(H){=}CH_2](\mu\text{-}H)$, **1** (38% yield) and $Os_2(CO)_6[\mu\text{-}\eta^4\text{-}S(CH_2)_3CH{=}CHCH_2](\mu\text{-}H)$, **2** (27% yield) after 48 h. Both products were characterized by single-crystal X-ray diffraction analysis. Compound **1** contains a triangular triosmium cluster with ten linear terminal carbonyl ligands, a hydride ligand and a hexadienethiolate ligand. Compound **2** contains only two mutually bonded osmium atoms, six linear terminal carbonyl ligands and a hexenylthiolate ligand that bridges the two osmium atoms via a bridging sulfur atom and three of the carbon atoms at the C-terminus of the hexenyl group. Ring opening of VTHT by a triosmium cluster occurs exclusively at the vinyl-substituted carbon atom. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tetrahydrothiophene; Ring-opening; Substituent effects; Osmium

1. Introduction

The removal of sulfur from organosulfur impurities is the most important first step in purification of petroleum feedstocks. The commercial process, known as hydrodesulfurization, involves a combination of hydrogen addition and sulfur removal upon the cleavage of the carbon–sulfur bonds from the sulfur containing heterocycles found in petroleum crude [1–4]. Thiophene and related aromatic heterocycles are among the most difficult compounds to desulfurize, and these are widely used as models to study the chemical reactions involved. Although there are numerous examples of the direct insertion of metal atoms into the carbon–sulfur bonds of thiophene and related compounds [4], many have suggested that hydrogen additions to the unsaturated sulfur heterocycles may play a key role in the desulfurization process [1,5a]. As a result, the desulfurizations of hydrogenated thiophenes, such as dihydro- and tetrahydrothiophene (THT) have also been widely studied [6].

In recent work, we have been investigating ring-opening transformations of strained, saturated, sulfur-containing heterocycles that are coordinated to polynuclear metal complexes [7,8]. We have found that bridging coordination of the sulfur atom promotes cleavage of the carbon–sulfur bonds by nucleophilic addition reactions [7]. However, spontaneous carbon–sulfur bond cleavages by insertion of metal atoms into carbon–sulfur bonds have also been observed [8]. Boorman et al. have shown that certain nucleophiles will even cleave the carbon–sulfur bonds of unstrained sulfur heterocycles when the sulfur atom bridges two tungsten atoms [9].

We have shown that tetrahydrothiophene undergoes spontaneous ring opening upon mild heating when it is coordinated to a triosmium cluster. A 2-butenethiolate ligand was formed by a combination of C–S and C–H bond cleavages [10].

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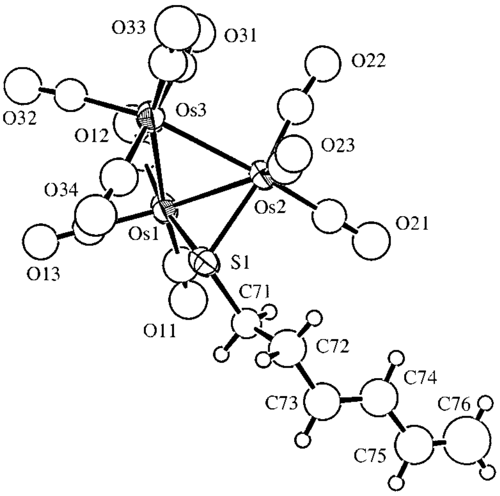
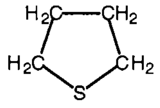
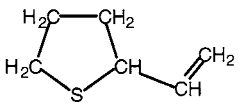


Fig. 1. An ORTEP diagram of the molecular structure $Os_3(CO)_{10}$[μ-$SCH_2CH_2C(H)=C(H)C(H)=CH_2$](μ-H), **1** showing 50% probability thermal ellipsoids.

We have recently discovered that vinyl substituents facilitate the ring opening of thiiranes [11]. We are unaware of any studies of the effects of vinyl-substituents on the ring-opening reactions of simple substituted tetrahydrothiophenes. Accordingly, we have proceeded to investigate the effect of a vinyl substituent on the ring-opening process. In this report, the results of our investigations of the ring opening to 2-vinyltetrahydrothiophene VTHT at a triosmium center are described.



THT



VTHT

2. Results

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with VTHT, at 25°C yielded two products formulated as $Os_3(CO)_{10}$[μ-$SCH_2CH_2C(H)=C(H)C(H)=CH_2$](μ-H), **1** (38%) and $Os_2(CO)_6$[μ-η^4-$S(CH_2)_3CH=CHCH_2$](μ-H), **2** (27%) after 48 h. Both products were characterized by a combination of IR, ^{1}H-NMR and single-crystal X-ray diffraction analyses.

Compound **1** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of these is shown in Fig. 1. Selected bond distances and angles are listed in Tables 1 and 2, respectively. Compound **1** contains a triangular triosmium cluster with ten linear terminal carbonyl ligands. There is a hexadienethiolate ligand coordinated to one edge of the cluster through the sulfur atom, Os(1)–S(1) = 2.41(1) Å and Os(2)–S(1) = 2.41(1) Å [Os(4)–S(2) = 2.42(1) Å and Os(5)–S(2) = 2.42(1) Å]. These Os–S distances are similar to those found for other bridging thiolate–triosmium linkages that have been structurally characterized [12]. The unsaturation in the hydrocarbon chain lies in the four carbon atoms that are the most remotely positioned from the sulfur atom and is verified by the shortness of the carbon–carbon bonds, C(73)–C(74) = 1.36(6) Å and C(75)–C(76) = 1.31(7) Å, [C(83)–C(84) = 1.26(6) Å and C(85)–C(86) = 1.28(9) Å]. There is an *E*-stereochemistry at the internal C=C double bond. The unsaturation was further supported by the five olefinic resonances: $\delta = 6.28$ (dt, $J_{H-H} = 17$ Hz, $J_{H-H} = 10$ Hz, 1H) and 6.09 (dd, $J_{H-H} = 10.4$ Hz, $J_{H-H} = 15$ Hz, 1H), 5.63 (dt, $J_{H-H} = 15$ Hz, $J_{H-H} = 6.8$ Hz, 1H), 5.14 (d, $J_{H-H} = 17$ Hz, 1H), 5.03 (d, $J_{H-H} = 10.4$ Hz, 1H) observed in the ^{1}H-NMR spectrum. There is one hydride ligand as indicated by a highly shielded proton resonance, $\delta = -17.40$ ppm, that is characteristic of these ligands. The hydride ligand was not located in the

Table 1
Selected intramolecular distances for **1**[a]

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Os(1)	Os(2)	2.868(2)	Os(4)	Os(5)	2.861(2)
Os(1)	Os(3)	2.862(3)	Os(4)	Os(6)	2.864(3)
Os(2)	Os(3)	2.869(3)	Os(5)	Os(6)	2.861(2)
Os(1)	S(1)	2.41(1)	Os(4)	S(2)	2.42(1)
Os(2)	S(1)	2.41(1)	Os(5)	S(2)	2.42(1)
S(1)	C(71)	1.80(4)	S(2)	C(81)	1.88(5)
C(71)	C(72)	1.50(6)	C(81)	C(82)	1.51(6)
C(72)	C(73)	1.53(7)	C(82)	C(83)	1.61(7)
C(73)	C(74)	1.34(6)	C(83)	C(84)	1.26(6)
C(74)	C(75)	1.44(7)	C(84)	C(85)	1.42(8)
C(75)	C(76)	1.31(7)	C(85)	C(86)	1.28(9)
O	C(av)	1.18(5)			

[a] Estimated S.D.s in the least significant figure are given in parentheses.

Table 2
Intramolecular bond angles for **1**[a]

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
Os(2)	Os(1)	Os(3)	60.10(6)	Os(5)	Os(4)	Os(6)	59.97(6)
Os(1)	Os(2)	Os(3)	59.84(6)	Os(4)	Os(5)	Os(6)	60.07(6)
Os(1)	Os(3)	Os(2)	60.06(6)	Os(4)	Os(6)	Os(5)	59.95(6)
Os(2)	Os(1)	S(1)	53.5(2)	Os(4)	Os(5)	S(2)	53.7(2)
Os(3)	Os(1)	S(1)	81.8(3)	Os(5)	Os(4)	S(2)	53.8(3)
Os(1)	Os(2)	S(1)	53.4(3)	Os(6)	Os(4)	S(2)	81.1(3)
Os(3)	Os(2)	S(1)	81.6(3)	Os(6)	Os(5)	S(2)	81.2(3)
Os(1)	S(1)	Os(2)	73.1(3)	Os(4)	S(2)	Os(5)	72.5(3)
Os	C	O(av)	175(5)				

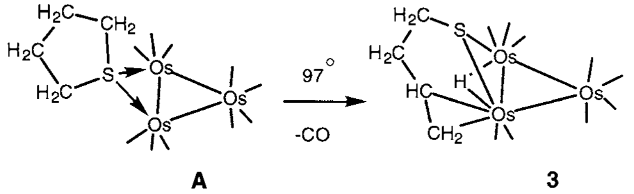
[a] Estimated S.D.s in the least significant figure are given in parentheses.

structural analysis, but is proposed to occupy a bridging position on the sulfur-bridged Os–Os bond on the other side of the cluster as found in related complexes [12].

Compound **2** crystallized with only one molecule in the asymmetric crystal unit. An ORTEP diagram of the molecular structure of **2** is shown in Fig. 2. Selected bond distances and angles are listed in Tables 3 and 4, respectively. Compound **2** contains only two metal atoms which are mutually bonded, Os(1)–Os(2) = 2.8591(9) Å. Each metal has three linear terminal carbonyl ligands. There is a hexenylthiolate ligand that bridges the two osmium atoms. It is coordinated via a bridging sulfur atom, Os(1)–S(1) = 2.410(4) Å and Os(2)–S(1) = 2.415(5) Å, and three of the carbon atoms C(4)–C(5)–C(6) at the C-terminus which also bridge the two metal atoms. Atoms C(4) and C(5) interact principally with Os(1), Os(1)–C(4) = 2.28(2) Å and Os(1)–C(5) = 2.59(2) Å while C(6) is bonded only to Os(2), Os(2)–C(6) = 2.25(2) Å. There is a weak, but still significant interaction between C(5) and Os(2), Os(2)–C(5) = 2.65(2) Å. The coordination of this three carbon group is similar to that found for μ-η^3-allyl ligands [13].

3. Discussion

In our previous studies, the complex $Os_3(CO)_{10}(THT)_2$ was shown to eliminate one of the THT ligands, one CO ligand and transform the other THT ligand into a 2-butenethiolate ligand in the triosmium cluster complex $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH{=}CH_2)(\mu\text{-}H)$, **3** when heated to 97°C [10]. Compound **3** was proposed to have been derived from an unobserved intermediate **A** containing a bridging THT ligand, Eq. (1). The transformation of **A** involved the loss of the CO ligand, cleavage of a hydrogen atom from one of the carbon atoms β to the sulfur atom and an opening of the ring by cleavage of one of the carbon–sulfur bonds.



(1)

Two products **1** and **2** were formed in the reaction of VTHT with $Os_3(CO)_{10}(NCMe)_2$. Both contain thiolate ligands that were clearly formed by opening of the ring of VTHT by cleavage of one of the carbon–sulfur bonds. In the formation of **1**, a hydrogen atom was also cleaved from the carbon atom adjacent to the vinyl substituted carbon of VTHT. This hydrogen atom became the hydride ligand on the cluster, and the VTHT ligand was converted into the hexadienethiolate ligand. In comparison to our previous study of the ring opening of THT by the triosmium cluster, we propose that an unobserved intermediate **B** containing a ligand of VTHT with a bridging sulfur atom may be involved prior to the ring-opening step, see Eq. (2).

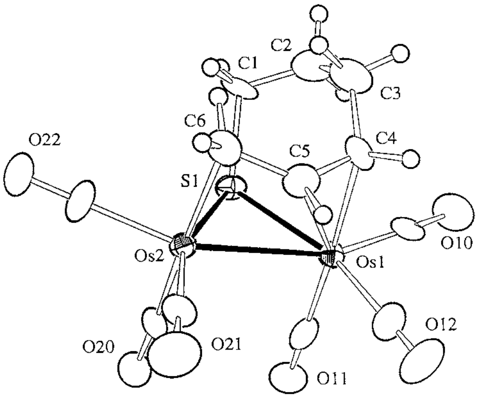
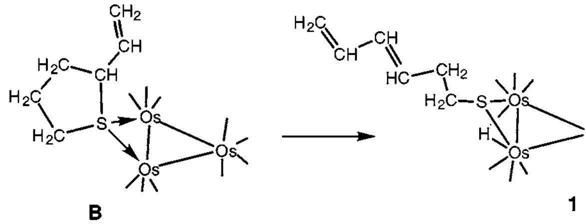


Fig. 2. An ORTEP diagram of the molecular structure of $Os_2(CO)_6[\mu\text{-}\eta^4\text{-}S(CH_2)_3CH{=}CHCH_2](\mu\text{-}H)$, **2** showing 50% probability thermal ellipsoids.

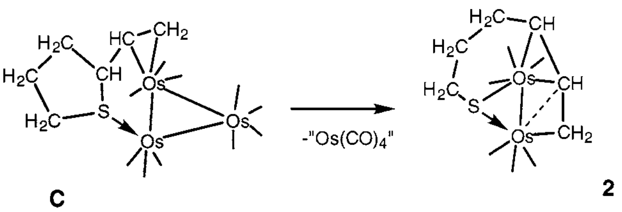
Table 3
Intramolecular distances for **2**[a]

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Os(1)	Os(2)	2.8591(9)	Os(2)	C(20)	1.91(2)
Os(1)	S(1)	2.410(4)	Os(2)	C(21)	1.87(2)
Os(1)	C(4)	2.28(2)	Os(2)	C(22)	1.92(2)
Os(1)	C(5)	2.59(2)	S(1)	C(1)	1.84(2)
Os(1)	C(10)	1.87(2)	O	C(av)	1.14(2)
Os(1)	C(11)	1.92(3)	C(1)	C(2)	1.47(4)
Os(1)	C(12)	1.92(2)	C(2)	C(3)	1.56(3)
Os(2)	S(1)	2.415(5)	C(3)	C(4)	1.49(3)
Os(2)	C(5)	2.65(2)	C(4)	C(5)	1.45(3)
Os(2)	C(6)	2.25(2)	C(5)	C(6)	1.42(3)

[a] Estimated S.D.s in the least significant figure are given in parentheses.



(2)



(3)

The formation of **2**, on the other hand, clearly proceeds by a different ring-opening mechanism. In support of this we also observed, in an independent test, that **1** is not converted to **2** under the conditions of the original synthesis. Overall, the formation of **2** involved the elimination of the two NCMe ligands, the addition of one equivalent of VTHT, cleavage of the carbon–sulfur bond to the vinyl-substituted carbon atom of VTHT, and the elimination of an $Os(CO)_4$ group from $Os_3(CO)_{10}(NCMe)_2$. One possible mechanism for this could involve loss of the two NCMe ligands and the addition of VTHT to the osmium cluster with coordination of the vinyl group and the sulfur atom using only one of the lone pairs of electrons on the sulfur atom. This intermediate could exhibit a structure such as **C** where the ligand occupies either diaxial or diequatorial coordination sites, see Eq. (3). The elimination of the $Os(CO)_4$ group could induce the cleavage of the carbon–sulfur bond, and the vinyl group and its adjacent carbon atom become coordinated to the two remaining osmium atoms in an η^3-bridging fashion.

A significant feature of the ring-opening transformations of VTHT by the triosmium cluster is that they occur under milder conditions than that of THT itself and in both cases it is the carbon–sulfur bond to the vinyl-substituted carbon atom that is cleaved. It will be interesting to see if other substituents also exhibit such a strong directing effect toward the opening of five-membered thioether rings.

4. Experimental

4.1. General data

Reagent grade solvents were dried by using sodium-benzophenone followed by distillation and were either used immediately or stored over 4 Å molecular sieves. 2-Vinyltetrahydrothiophene (VTHT) [14] and $Os_3(CO)_{10}(NCMe)_2$ [15] were prepared by the published procedures. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^{1}H-NMR spectra were run on either a Brüker AM-300 or Varian Mercury-400 spectrometer operating at 300 and 400 MHz, respectively. Chromatographic separations were performed in air on silica gel by using Analtech (0.25 mm) F_{254} uniplates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

4.2. Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-vinyltetrahydrothiophene

A 100-mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.107 mmol) and 27.0 µl (0.235 mmol) VTHT were dissolved in 25 ml of CH_2Cl_2 at 25°C. After stirring for 48 h, the solvent was removed in vacuo and the residue was separated by TLC using pure hexane as eluant. The following compounds were isolated in order of elution: $Os_2(CO)_6[\mu\text{-}\eta^4\text{-}SCH_2CH_2CH_2CHC(H){=}CH_2]$, **2**, (19.4 mg, 27%) and $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2C(H){=}C(H)\text{-}C(H){=}CH_2](\mu\text{-}H)$, **1**, (39.7 mg, 38%). Spectral data for **1**: IR νCO (cm^{-1} in hexane): 2109 (m), 2068 (vs), 2059

Table 4
Intramolecular bond angles for **2**[a]

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
Os(2)	Os(1)	S(1)	53.6(1)	Os(2)	Os(1)	C(4)	87.0(5)
S(1)	Os(2)	C(6)	90.6(5)	Os(2)	Os(1)	C(5)	57.9(5)
S(1)	Os(1)	C(4)	89.1(5)	Os(1)	S(1)	Os(2)	72.7(1)
S(1)	Os(1)	C(5)	85.2(4)	Os(1)	S(1)	C(1)	113.1(6)
Os(2)	S(1)	C(1)	114.6(6)	S(1)	C(1)	C(2)	114(2)
Os(1)	Os(2)	C(6)	85.1(5)	C(2)	C(3)	C(4)	122(2)
Os(1)	C(5)	C(6)	117(1)	C(3)	C(4)	C(5)	119(2)
Os(2)	C(5)	C(4)	118(1)	C(4)	C(5)	C(6)	125(2)
Os(2)	C(6)	C(5)	90(1)	Os	C	O(av)	178(2)

[a] Estimated S.D.s in the least significant figure are given in parentheses.

(s), 2025 (vs), 2019 (s), 1999 (s), 1990 (m), 1983 (m). ^{1}H=NMR (δ in $CDCl_3$): 6.28 (dt, $J_{\text{H-H}} = 17$ Hz, $J_{\text{H-H}} = 10$ Hz, 1H), 6.09 (dd, $J_{\text{H-H}} = 10.4$ Hz, $J_{\text{H-H}} = 15$ Hz, 1H), 5.63 (dt, $J_{\text{H-H}} = 15$ Hz, $J_{\text{H-H}} = 7$ Hz, 1H), 5.14 (d, $J_{\text{H-H}} = 17$ Hz, 1H), 5.03 (d, $J_{\text{H-H}} = 10.4$ Hz, 1H), 2.39 (m, 4H), -17.40 (s, 1H). Anal. Calc. for **1**: C, 19.94; H, 0.94; found C, 20.37; H, 0.86. Spectral data for **2**: IR νCO (cm^{-1} in hexane): 2081 (m), 2051 (vs), 2002 (s), 1988 (vs), 1980 (m). ^{1}H-NMR (δ in $CDCl_3$): 5.14 (dt, $J_{\text{H-H}} = 12$ Hz, $J_{\text{H-H}} = 8$ Hz, 1H), 3.40 (tt, $J_{\text{H-H}} = 9$ Hz, $J_{\text{H-H}} = 2$ Hz, 1H), 2.63 (m, 1H), 1.99 (ddd, $J_{\text{H-H}} = 2$ Hz, $J_{\text{H-H}} = 6$ Hz, $J_{\text{H-H}} = 8$ Hz, 1H), 1.86 (m, 2H), 1.12 (tt, $J_{\text{H-H}} = 3$ Hz, $J_{\text{H-H}} = 14$ Hz, 1H), 0.84 (m, 3H). Anal. Calc. for **2**: C, 21.75; H, 1.52; found C, 21.31; H, 1.32.

4.3. Crystallographic analyses

Crystals of **1** and **2** suitable for X-ray diffraction measurements were obtained by slow evaporation of solvent from solutions in hexane at 25°C. The crystals used in data collection 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$_\alpha$ radiation. The unit cells were 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 5. All data processing was performed on a Silicon Graphic Indigo^2 computer 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 [16a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [16b]. Full matrix least-squares refinements minimized the function: $\Sigma_{hkl}\, w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.06 I_{net})^2]^{1/2}/L_p$.

Compounds **1** and **2** both crystallized in the monoclinic crystal system. The space groups $P2_1/a$ and $P2_1/n$, respectively, were identified on the basis of the systematic absences observed in the intensity data and the successful solution and refinement of the structures. Both structures where solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Absorption corrections were applied in both analyses. However, the crystals of compound **1** grew as very thin plates. An empirical correction was applied

Table 5
Crystallographic data for compounds **1** and **2**[a]

Compound	**1**	**2**
Formula	$Os_3SO_{10}C_{16}H_{10}$	$Os_2SO_6C_{12}H_{10}$
Formula weight	964.91	662.67
Crystal system	Monoclinic	Monoclinic
Lattice parameters		
a (Å)	16.982(4)	8.353(1)
b (Å)	14.410(9)	12.419(2)
c (Å)	20.604(6)	14.812(2)
α (°)	90	90
β (°)	113.24(2)	92.145(12)
γ (°)	90	90
V (Å^3)	4633(3)	1535.6(3)
Space group	$P2_1/a$(# 14)	$P2_1/n$(# 14)
Z value	8	4
$D_{\text{calc.}}$ (g cm^{-3})	2.77	2.87
μ (Mo–K$_\alpha$) (cm^{-1})	165.6	166.8
Temperature (°C)	20	20
$2\Theta_{\max}$ (°)	40	45
No. of observations ($I > 3\sigma(I)$)	2233	1611
No. of variables	282	190
Goodness-of-fit	1.63	1.45
Maximum shift in final cycle	0.02	0.01
Residuals: R; R_w	0.055; 0.082	0.044; 0.059
Abs. Cor.	Empirical	DIFABS
Transmission coeffecient (max/min)	1.000–0.077	1.00–0.44
Largest peak in final different four. (e Å^{-3})	2.58	1.64

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

(based on psi scans) but the quality of the structure was still limited by serious absorption effects and by relatively low amounts of observed data due to the small size of the crystal and the presence of two independent molecules in the asymmetric crystal unit. For **1** only the osmium and sulfur atoms were refined with anisotropic thermal parameters. For **2** all non-hydrogen atoms were refined with anisotropic thermal parameters. For both analyses the hydrogen atom positions on the ligands were calculated by assuming idealized geometries, C–H = 0.95 Å. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The hydride ligand on compound **1** could not be located and was ignored in the analysis.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 113686 and 113687 for compounds **1** and **2**, respectively. 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 www: http://www.ccdc.cam.ac.uk].

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