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Note

# Synthesis of new thiol derivatives of $[Os_3(CO)_{12}]$ ; crystal structure of $[Os_3(CO)_{10}(\mu-H){\mu-SC(CH_3)_3}]$

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#### Abstract

The clusters  $[Os_3(CO)_{10}(\mu-H){\mu-SC(CH_3)_3}]$  (1) and  $[Os_3(CO)_{10}(\mu-H){\mu-SC_6H_{11}}]$  (2) have been synthesized by addition of the appropriate thiol RSH (R=C(CH\_3)\_3, C\_6H\_{11}) to  $[Os_3(CO)_{11}(NCMe)]$  or  $[Os_3(CO)_{10}(NCMe)_2]$  in dichloromethane. Clusters 1 and 2 have been characterized by IR, NMR, mass spectrometry and, in the case of 1, X-ray crystallography. Compound 1 crystallizes in space group  $P2_1/n$  (a=9.507(1), b=12.860(1), c=17.838(3) Å,  $\beta$ =99.77(1)°, Z=4). The molecule conforms to an idealized C, symmetry. The bond distances in the osmium triangle average 2.860 Å; there is no significant elongation of the Os-Os edge in 1 that is bridged by the hydride and the thiolate moiety.

Keywords: Cluster complexes; Crystal structures; Thiolate complexes; Osmium complexes; Carbonyl complexes; Hydride complexes

#### 1. Introduction

The coordination modes of ligands to metal clusters are often similar to those found on metal surfaces [1]. A better understanding of transformations undergone by ligands on the clusters can give useful information which may aid the elucidation of similar reaction pathways on heterogeneous catalysts/metal surfaces. Sulfur-containing ligands have been the subject of intensive investigation in this context [2]. The study of the mechanism(s) of transition metal catalyzed hydrodesulfurization (HDS) of thiols, thioethers and thiophenes has received much attention in recent years [3] and several mono-, di- and polynuclear metal complexes containing sulfur ligands have been synthesized as both structural and functional models for HDS processes [4].

The interaction and desulfurization of thiols with metal (molybdenum) surfaces have been presented by Friend et al. [5]. The cleavage of the sulfur-hydrogen bond to form a metal-bound thiolate has been found to be rapid whereas the cleavage of the carbon-sulfur bond appears to be the ratelimiting step. In this context, we are currently studying whether it is possible to monitor the initial coordination of thiols to polynuclear metal complexes, in particular the trinuclear metal carbonyl clusters of the iron triad. In the course

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of these investigations, we have isolated new thiol derivatives of  $[Os_3(CO)_{12}]$ , viz.  $[Os_3(CO)_{10}(\mu-H) \{\mu-SC(CH_3)_3\}]$ (1) and  $[Os_3(CO)_{10}(\mu-H) \{\mu-SC_6H_{11}\}]$  (2).

## 2. Results and discussion

Addition of the appropriate thiol RSH  $(R = C(CH_3)_3, C_6H_{11})$  to  $[Os_3(CO)_{11}(NCMe)]$  or  $[Os_3(CO)_{10}(NCMe)_2]$ in dichloromethane at room temperature resulted in the rapid formation of  $[Os_3(CO)_{10}(\mu-H)(\mu-SR)]$  in high yields. The existence of hydrides was unambiguously proven by their upfield-shifted <sup>1</sup>H NMR resonances. In addition, the resemblance of the IR spectra of 1 and 2 to those of previously synthesized  $[Os_3(CO)_{10}(\mu-H)(SR)]$  clusters [6] provided strong evidence that, in both cases, one Os–Os bond is bridged by  $\mu_2$ -hydride and thiolate bridges. In the case of 1, this has been proven through the determination of its molecular structure by single crystal X-ray crystallography.

The molecular structure of  $[Os_3(CO)_{10}(\mu-H){\mu-SC-(CH_3)_3}]$  (1) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The osmium atoms define an isosceles triangle; the Os(1)-Os(3) distance is 2.8588(5) Å and the Os(2)-Os(3) distance is 2.8553(6) Å. The metalmetal distance of the third edge (Os(1)-Os(2) 2.8654(5) Å), which is spanned by the  $\mu$ -SC(CH<sub>3</sub>)<sub>3</sub> moiety and the hydride, is slightly – but not significantly – larger than

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Fig. 1. ORTEP [7] drawing of  $[Os_3(CO)_{10}(\mu-H)\{\mu-SC(CH_3)_3\}]$  (1) showing thermal ellipsoids at 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for 1

$U_{S(2)} = U_{S(3)} = U_{S(1)}$	00.19(1)	Us(3) - Us(2) - Us(1)	) סע.עכ
C(10) - Os(3) - Os(1)	86.6(3)	$O_{s}(3) - O_{s}(1) - O_{s}(2)$	59.84(2)
C(6)-Os(2)-Os(1)	115.2(3)	C(10) - Os(3) - Os(2)	86.7(3)
C(4)-Os(2)-S	99.0(3)	C(2) - Os(1) - Os(2)	114.7(3)
C(2)-Os(1)-S	166.6(3)	C(3)-Os(1)-S	100.2(3)
C(14)-C(11)-S	104.0(7)	C(6)-Os(2)-S	168.5(3)
C(12)-C(11)-S	104.2(7)	C(13)-C(11)-S	116.0(7)
C(8)-Os(3)-C(9)	102.2(5)	C(8)-Os(3)-Os(2)	97.4(3)
Os(2)-S-Os(1)	72.92(6)	C(9)-Os(3)-Os(1)	100.2(3)
Os(2)-H(1)	1.83 *		
Os(3)-C(10)	1.97(1)	Os(1) - H(1)	1.83 *
Os(3)-C(8)	1.93(1)	Os(3) - C(9)	1.93(1)
Os(3)-C(7)	1.96(1)	C(10)-O(10)	1.11(1)
Os(2)-C(6)	1.90(1)	C(9)-O(9)	1.13(1)
Os(2) - C(4)	1.91(1)	C(8)-O(8)	1.14(1)
$O_{s(2)}-C(5)$	1.91(1)	C(7)-O(7)	1.12(1)
Os(1) - C(3)	1.93(1)	C(6)-O(6)	1.13(1)
Os(1) - C(2)	1.89(1)	C(5)-O(5)	1.13(1)
$O_{s(1)}-C(1)$	1.91(1)	C(4)-O(4)	1.14(1)
S-C(11)	1.881(9)	C(3)-O(3)	1.11(1)
Os(2)-S	2.411(2)	C(2)-O(2)	1.14(1)
Os(1)-S	2.411(2)	C(1)-O(1)	1.13(1)
Os(2) - Os(3)	2.855(1)	C(11)-C(12)	1.51(2)
Os(1) - Os(3)	2.859(1)	C(11)-C(13)	1.52(2)
Os(1) - Os(2)	2.865(1)	C(11)-C(14)	1.51(2)

\* Values calculated using XHYDEX [8].

those of the other two edges. All three Os–Os interactions (Os–Os av. 2.860 Å) are shorter than those found in the parent binary carbonyl  $[Os_3(CO)_{12}]$  (Os–Os av. 2.877(3) Å) [9]. The two equal Os–S bond lengths (2.411(2) Å) lie in the range which is typical for bridging thiolato ligands in triosmium cluster complexes (2.40–2.46 Å) [10]. Although the steric bulk of the tert-butyl moiety is considerably larger than that of the corresponding ethanethiol moiety of  $[Os_3CO)_{10}(\mu$ -H)( $\mu$ -SEt)] [11], the Os-Os distances for 1 are similar to those observed in the latter cluster (Os-Os av. 2.854 Å) and the dihedral angles between the metal and Os-S-Os triangles of 1 and  $[Os_3CO)_{10}(\mu$ -H)-( $\mu$ -SEt)] are virtually identical (76°).

The hydride has not been directly located in the electron density map but the large angles for the *cis* carbonyl ligands  $(Os(2)-Os(1)-C(2) \quad 114.7(3)^\circ, \quad Os(1)-Os(2)-C(6)$  $115.2(3)^\circ$ ) indicate that the hydride is bridging the Os(1)-Os(2) bond. It has therefore been assigned to bridge the same edge as the  $-SC(CH_3)_3$  moiety and its position has been calculated using the XHYDEX program [8]. The molecule possesses an idealized  $C_s$  symmetry with the pseudomirror plane passing through Os(3), S, C(11), C(13), C(7), O(7), C(10), O(10) but there are some distortions which are probably due to packing effects.

It is plausible that the above-mentioned thiols initially coordinate in a terminal fashion but no intermediate could be detected by IR or NMR spectroscopy. The addition of these and other thiols to trinuclear clusters will be studied using rapid detection methods.

# 3. Experimental

All reactions were carried out at room temperature under nitrogen using standard Schlenk techniques. All solvents were dried over appropriate drying agents and distilled before use. IR spectra were recorded on a Nicolet 20 SXC FT-IR spectrometer, fast atom bombardment mass spectra on a Jeol SX-102 spectrometer and <sup>1</sup>H NMR spectra on a Varian UNITY 300 MHz spectrometer using CDCl<sub>3</sub> as the internal reference. Products were separated in air by TLC on 20×20 cm glass plates coated with a 0.25 mm layer of Merck Kieselgel 60, using n-hexane–CH<sub>2</sub>Cl<sub>2</sub> (10:1, vol./vol.) as eluent. The clusters  $[Os_3(CO)_{11}(NCMe)]$  and  $[Os_{3}-(CO)_{10}(NCMe)_2]$  were prepared by literature methods [12].

# 3.1. Syntheses of $[Os_3(CO)_{10}(\mu-H)(\mu-SR] (R = C(CH_3)_3 (1), C_6H_{11}(2))$

# 3.1.1. $[Os_3(CO)_{10}(\mu-H){\mu-SC(CH_3)_3}](1)$

A total of 0.11 mmol of  $(CH_3)_3CSH$  was added by syringe to a solution of  $[Os_3(CO)_{11}(NCMe)]$  (100 mg, 0.11 mmol) in  $CH_2Cl_2$  (20 cm<sup>3</sup>). The solution changed from yellow to bright yellow upon addition of the thiol. The reaction was monitored by IR spectroscopy and judged to be complete after 1 h; the solvent was subsequently removed under reduced pressure. TLC of the residue gave a first yellow fraction containing  $Os_3(CO)_{12}$  in trace amount, followed by a second yellow fraction containing  $[Os_3(CO)_{10}(\mu-H){\mu-SC(CH_3)_3}]$  (1) in 90% yield. Cluster 1 was crystallized from a  $CH_2Cl_2/n$ -hexane mixture at -20 °C.

Table 3

In a similar reaction,  $(CH_3)_3CSH$  was added to a solution of  $[Os_3(CO)_{10}(NCMe)_2]$  (100 mg, 0.11 mmol) in  $CH_2Cl_2$ (20 cm<sup>3</sup>) and the reaction was stopped after 1 h. Work-up as above afforded  $[Os_3(CO)_{10}(\mu-H){\mu-SC(CH_3)3}]$  (1) in 95% yield. IR  $(CH_2Cl_2)$ :  $\nu(CO)$  2108w, 2064vs, 2056s, 2021vs, 1993m. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 0.75 (s, SC(CH<sub>3</sub>)<sub>3</sub>, -17.90 (s, Os( $\mu$ -H)). FAB-MS ( $M^+$ , m/z(a.m.u.)): 940 (calc.), 940 (found).

## 3.1.2. $[Os_3(CO)_{10}(\mu-H){\mu-SC_6H_{11}}](2)$

A slight excess of  $C_6H_{11}SH$  was added by a syringe to a solution of  $[Os_3(CO)_{11}(NCMe)]$  (100 mg, 0.11 mmol) in  $CH_2Cl_2$  (20 cm<sup>3</sup>) and the reaction mixture was allowed to stir for 5 h at room temperature. Removal of the solvent and subsequent TLC afforded  $[Os_3(CO)_{10}(\mu-H)\{\mu-SC_6H_{11}\}]$  (2) in 85% yield.

Similarly,  $[Os_3(CO)_{10}(NCMe)_2]$  (100 mg, 0.11 mmol) was stirred with a slight excess of cyclohexanethiol for 5 h. Removal of the solvent and purification by TLC afforded compound 2 in 80% yield.

IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 2107m, 2065vs, 2057s, 2020s, 1995m. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 1.24–2.03 (m, (SC<sub>6</sub>H<sub>11</sub>)), -17.63 (s, Os( $\mu$ -H). FAB-MS ( $M^+$ , m/z(a.m.u.)): 966 (calc.), 966 (found).

#### 3.2. X-ray structure determination

A yellow rectangular prism of 1 was mounted on a glass fiber, placed in a goniometer head on an Enraf-Nonius

#### Table 2

Crystal data and details of measurements for  $[Os_3(CO)_{10}(\mu-H){\mu-SC-(CH_3)_3}](1)$ 

Formula	C.H.O.Os2S
M	940.88
Crystal size (mm)	0.20×0.25×0.30
Temperature (°C)	25
System	monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å	9.507(1)
b (Å)	12.860(1)
c (Å)	17.838(3)
β(°)	99.77(1)
V (Å <sup>3</sup> )	2149.2(5)
Z	4
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	2.908
F(000)	1672
Radiation (graphite monochromated), $\lambda$ (Å)	Μο Κα, 0.71067
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	17.834
Scan mode	ω
θ Range (°)	2-30
Reflections collected	6567
Unique observed reflections $(I > 2\sigma(I))$	6205
No. of refined parameters	256
$R(F) (I > 2\sigma(I))$	0.0340
$wR(F^2)$	0.0708
$S(F^2)$	0.991

 $R(F) = \sum |F_o - F_c| / \sum |F_o|; wR(F^2) = \sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2; S(F^2)$ =  $\sum w(F_o^2 - F_c^2)^2 / (N_D - N_P), N_D$  = no. of data,  $N_P$  = no. of parameters.

Fractional atomic coordinates  $(\times 10^4)$  for  $[Os_3(CO)_{10}(\mu-H){\mu-SC-(CH_3)_3}(1)$ 

	x	у	z
Os(1)	1742(1)	2994(1)	6963(1)
Os(2)	-1028(1)	3249(1)	6057(1)
Os(3)	-758(1)	2443(1)	7566(1)
S	663(2)	1890(2)	5931(1)
C(1)	2766(11)	1884(7)	7520(5)
O(1)	3326(9)	1215(7)	7854(5)
C(2)	2141(10)	3904(9)	7805(6)
O(2)	2439(9)	4444(7)	8318(5)
C(3)	3341(11)	3525(9)	6548(6)
O(3)	4309(9)	3846(8)	6362(6)
C(4)	-1108(11)	3897(8)	5089(5)
O(4)	-1302(10)	4314(6)	4519(4)
C(5)	-2649(11)	2370(8)	5767(6)
O(5)	- 3588(9)	1827(8)	5609(6)
C(6)	-2126(10)	4370(9)	6349(6)
O(6)	-2792(9)	5036(7)	6504(5)
C(7)	-615(11)	1033(8)	7175(6)
O(7)	-620(9)	195(6)	7006(5)
C(8)	-2768(12)	2291(9)	7592(6)
O(8)	- 3957(9)	2203(8)	7609(5)
C(9)	99(12)	1992(9)	8571(6)
O(9)	582(11)	1711(8)	9156(5)
C(10)	-796(13)	3900(10)	7906(6)
O(10)	- 852(10)	4711(7)	8103(6)
C(11)	1438(11)	1934(8)	5029(5)
C(12)	243(15)	1550(9)	4423(6)
C(13)	1940(14)	2991(9)	4805(6)
C(14)	2649(15)	1159(11)	5164(8)
H(1)	593	3983	6431

CAD 4 diffractometer and centered optically. The diffraction experiments were carried out at room temperature. The unit cell parameters were determined from 25 randomly selected reflections using automatic search, indexing and least-squares routines. Crystal data and details of the data collection for 1 are given in Table 2. Intensity measurements were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using the azimuthal scan method. The metal atom positions were determined by direct methods using SHELXS 86 [13]. Least-squares refinement and difference Fourier syntheses revealed all remaining non-H atoms. The position of the hydrogen atom bridging the Os(1)-Os(2) edge was calculated using the program XHY-DEX [8] and the methyl hydrogen atoms were included in idealized positions. All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were assigned an isotropic thermal parameter 1.3 times that of the attached carbon atom. All calculations were carried out using the program SHELXL 93 [14]. Final positional parameters with their estimated standard deviations are given in Table 3.

#### 4. Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Structure factors are available from the authors.

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