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$Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$: structural evidence for the transformation of pyridine-2-thione *N*-oxide to pyridine-2-thiolate in osmium complexes

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Abstract

The reaction of $Os_3(CO)_{12}$ with an excess of 1-hydroxypyridine-2-thione and Me_3NO gives three mononuclear osmium complexes $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**), $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**), and $Os(CO)_2(\eta^2\text{-}SC_5H_4N)_2$ (**3**). The results of single-crystal X-ray analyses reveal that complex **1** contains two *O,S*-chelate pyridine-2-thione *N*-oxide (PyOS) ligands, whereas complex **2** contains one *O,S*-chelate PyOS and one *N,S*-chelate pyridine-2-thiolate group. The unique structure of **2** provides evidence of the pathway for this transformation. When this reaction was monitored by ^1H NMR spectroscopy the triosmium complexes $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}S\text{-}C_5H_4N(O))$ (**4**) and $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SC_5H_4N(O))$ (**5**) were identified as intermediates in the formation of the mononuclear final products **1**–**3**. The proposed pathway is further supported by the observation of several dinuclear osmium intermediates by electrospray ionization mass spectrometry. In addition, the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the absence of Me_3NO at 90 °C generated mononuclear complex **2** as the major product along with smaller amounts of complexes **1** and **3**. These results suggest that the *N*-oxide facilitates the decarbonylation reaction. Crystal data for **1**: monoclinic, space group *C*2/*c*, $a = 26.9990(5)$ Å, $b = 7.6230(7)$ Å, $c = 14.2980(13)$ Å, $\beta = 101.620(2)°$, $V = 2882.4(4)$ Å^3, $Z = 8$. Crystal data for **2**: monoclinic, space group *C*2/*c*, $a = 5.7884(3)$ Å, $b = 13.9667(7)$ Å, $c = 17.2575(9)$ Å, $\beta = 96.686(1)°$, $V = 1385.69(12)$ Å^3, $Z = 4$.

Keywords: Osmium; Cluster; *N*-oxide ligand; Transformation; Crystal structure; Intermediate

1. Introduction

Metal complexes containing a heterocyclic thione ligand not only exhibit versatile structures but also possess biological activities; some of these complexes have the potential for important applications [1–8]. As a part of our research program of the study of rearrangement processes in a variety of fundamental reactions, we selected derivatives of triosmium dodecacarbonyl as model complexes because of the modest stability of the reaction intermediates and products [9,10]. Herein we report our new findings on the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione, in which the stepwise conversion of triosmium pyridine-2-thione *N*-oxide clusters into mononuclear osmium pyridine-2-thiolate complexes is observed. A comparison of the structures of

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three monomeric osmium products is of particular interest. The structural information obtained provides a piece of evidence that is useful for elucidating the transformation pathway of the reaction, which was further supported by NMR and ESI-MS analyses.

2. Results and discussion

2.1. Reaction of $Os_3(CO)_{12}$ with excess 1-hydroxypyridine-2-thione and Me_3NO

Treatment of $Os_3(CO)_{12}$ with an excess of 1-hydroxypyridine-2-thione in the presence of eight equivalents of Me_3NO in CH_2Cl_2 afforded three mononuclear osmium complexes $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**, 19%), $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**, 17%), and $Os(CO)_2(\eta^2\text{-}SC_5H_4N)_2$ (**3**, 1%, Scheme 1). Complexes **1**–**3** were isolated as yellow microcrystalline solids and were fully characterized spectroscopically. The FAB mass of **1** exhibited a molecular ion peak at *m*/*z* 500. The ^1H and ^{13}C NMR spectra indicated that the two pyridine-2-thione *N*-oxide ligands were equivalent. Their chemical shifts and resonance pattern are similar to those of the triosmium complex $Os_3(CO)_{10}(\mu\text{-}H)(\eta^2\text{-}S\text{-}C_5H_4N(O))$ reported previously [8c]. The two strong ν(CO) signals at 2025 and 1949 cm^{-1} in the IR spectrum indicate a *cis* dicarbonyl arrangement [11].

A single-crystal X-ray diffraction study of **1** was carried out to confirm the solid-state structure. An ORTEP drawing of **1** is shown in Fig. 1; relevant crystallographic details are listed in Tables 1 and 2. The geometry of **1** is essentially octahedral with a slight distortion because of the presence of two five-membered *O,S*-chelate pyridine-2-thione *N*-oxide rings. These two chelate ligands are arranged with two sulfur atoms *trans* and the two oxygen atoms *cis*. The two carbonyl groups are disposed in a *cis* arrangement and are *trans* to the oxygen atoms. The internal chelate angles, 82.41(9)° and 83.21(9)°, for S–Os–O in complex **1** are slightly larger than that (81.0(3)°) of the triosmium complex $Os_3(CO)_9(\mu\text{-}H)(CNPr)(\eta^2\text{-}SC_5H_4N(O))$ [8c]. The N–O bond distances (1.355(5) and 1.359(5) Å) in **1** are slightly longer than that (1.34(1) Å) of the coordinated *N*-oxide ligand

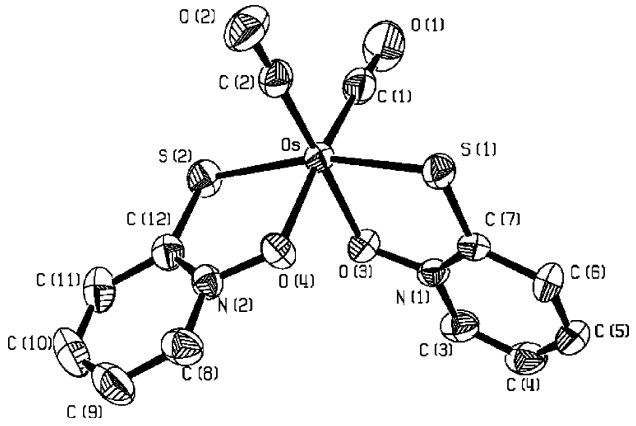
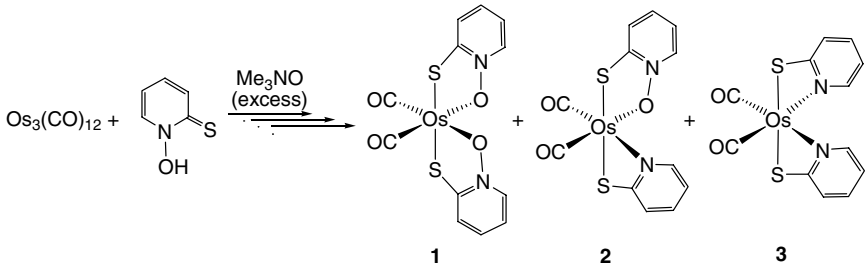


Fig. 1. ORTEP diagram of complex $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**).

in $Os_3(CO)_9(\mu\text{-}H)(CNPr)(\eta^2\text{-}SC_5H_4N(O))$ and that (1.30(2) Å) in a typical noncoordinated *N*-oxide [8c,12].

The ^1H NMR spectrum of **2** exhibits two sets of signals arising from the bidentate pyridine-2-thione *N*-oxide (PyOS) and pyridine-2-thiolate (PyS) ligands, respectively. The resonance pattern of the PyOS was similar to that of complex **1**, while the proton peaks of the PyS were similar to those of complex $Os(CO)_2(\eta^2\text{-}SC_5H_4N)_2$ (**3**) [13]. In order to obtain unambiguous information on its molecular stereochemistry, we determined the structure of **2** by X-ray diffraction. An ORTEP drawing is shown in Fig. 2. Crystallographic data are listed in Table 1, while selected bond distances and angles are given in Table 3. The coordination about the osmium atom is highly distorted octahedral resulting from the presence of one five-membered *O,S*-chelate pyridine-2-thione *N*-oxide ring and one four-membered *N,S*-chelate pyridine-2-thiolate ring. These two rings are disordered with respect to each other as related by a crystallographic twofold axis. The sulfur atoms in the pyridine-2-thiolate and the pyridine-2-thione *N*-oxide ligands are mutually *trans* and the two CO ligands are mutually *cis*. Most other mononuclear octahedral complexes with two chelate pyridine-2-thiolate (PyS) ligands also have a similar geometry, with the sulfur atoms in a *trans* arrangement [14].

Complex **3** exhibited identical data to those in the literature [13]. The pyridine-2-thiolate ligands are coor-



Scheme 1.

Table 1
Crystal and intensity collection data for $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**) and $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**)

	1	**2**
Formula	$C_{12}H_8N_2O_4OsS_2$	$C_{12}H_8N_2O_3OsS_2$
Fw	498.52	482.52
Space group	*C*2/*c*	*C*2/*c*
a (Å)	26.9990 (5)	5.7884 (3)
b (Å)	7.6230 (7)	13.9667 (7)
c (Å)	14.2980 (13)	17.2575 (9)
β (°)	101.620 (2)	96.686 (1)
V (Å^3)	2882.4 (4)	1385.7 (1)
D_{calc} (g cm^{-3})	2.298	2.313
Z	8	4
Cryst dimension (mm)	$0.34 \times 0.26 \times 0.26$	$0.12 \times 0.08 \times 0.05$
Absorption coefficient *μ* (Mo Kα) (mm^{-1})	9.152	9.510
Temperature	Room temperature	Room temperature
Radiation	Mo Kα	Mo Kα
2*θ* (max)	49.94	52.7
Scan type	*ω*/2*θ*	*ω*/2*θ*
Total number of reflections	2638	4718
Number of observed reflections $F_o > 2\sigma(F_o)$	2520	1424
Observed variables	191	133
R	0.0199	0.0682
wR (F^2)	0.0471	0.1631
Δ(*ρ*) (e Å^{-3})	0.662	3.815
Goodness-of-fit	1.038	1.189

Table 2
Selected bond distances and angles for $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**)

(a) Bond distances (Å)			
Os–C(1)	1.857(6)	Os–C(2)	1.857(5)
Os–O(3)	2.110(3)	Os–O(4)	2.085(3)
Os–S(2)	2.3724(13)	Os–S(1)	2.3557(13)
S(1)–C(7)	1.710(5)	S(2)–C(12)	1.717(5)
O(1)–C(1)	1.149(6)	O(2)–C(2)	1.144(6)
O(3)–N(1)	1.359(5)	O(4)–N(2)	1.355(5)
N(2)–C(12)	1.350(6)	N(2)–C(8)	1.355(6)
N(1)–C(3)	1.362(6)	N(1)–C(7)	1.352(6)
C(3)–C(4)	1.337(7)	C(4)–C(5)	1.389(8)
C(5)–C(6)	1.342(8)	C(6)–C(7)	1.417(7)
C(8)–C(9)	1.353(7)	C(9)–C(10)	1.370(9)
C(10)–C(11)	1.358(8)	C(11)–C(12)	1.405(7)
(b) Bond angles (°)			
C(1)–Os–C(2)	91.6(2)	C(1)–Os–O(3)	91.8(2)
C(2)–Os–O(3)	176.56(18)	C(1)–Os–O(4)	174.17(19)
C(2)–Os–O(4)	94.12(19)	O(3)–Os–O(4)	82.51(13)
C(1)–Os–S(2)	98.47(18)	C(2)–Os–S(2)	93.07(16)
O(3)–Os–S(2)	87.20(9)	O(4)–Os–S(2)	82.41(9)
C(1)–Os–S(1)	93.23(18)	C(2)–Os–S(1)	95.83(16)
O(3)–Os–S(1)	83.21(9)	O(4)–Os–S(1)	85.03(9)
S(2)–Os–S(1)	165.08(5)	C(7)–S(1)–Os	97.68(17)
C(12)–S(2)–Os	97.97(18)	N(1)–O(3)–Os	116.0(3)
N(2)–O(4)–Os	117.7(3)	C(12)–N(2)–O(4)	121.7(4)
C(12)–N(2)–C(8)	123.6(4)	O(4)–N(2)–C(8)	114.7(4)
C(3)–N(1)–C(7)	122.2(4)	C(3)–N(1)–O(3)	115.9(4)
C(7)–N(1)–O(3)	121.8(4)	N(1)–C(3)–C(4)	121.2(5)
N(1)–C(7)–C(6)	116.2(5)	N(1)–C(7)–S(1)	121.2(4)
C(6)–C(7)–S(1)	122.7(4)	N(2)–C(12)–C(11)	115.9(5)
N(2)–C(12)–S(2)	120.1(4)	C(11)–C(12)–S(2)	123.9(5)

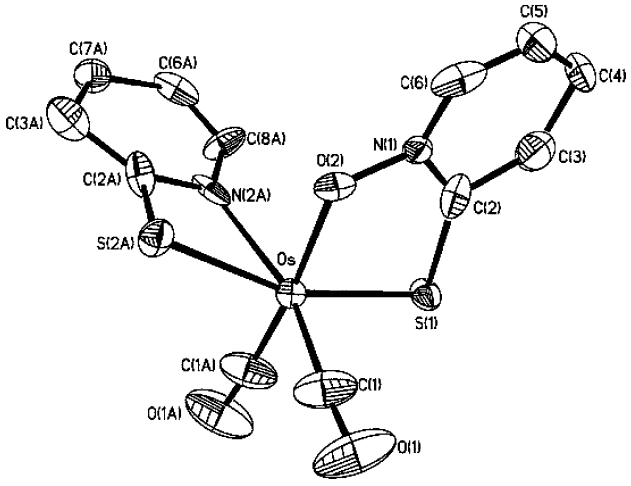


Fig. 2. ORTEP diagram of $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**).

dinated to the osmium center, forming two four-membered *N,S*-chelate PyS rings.

It is of particular interest to compare the structures of these three monomeric osmium products (Scheme 1). There are indeed a series of products containing two pyridine-2-thione *N*-oxide (PyOS) ligands in **1**, and then one PyOS and one pyridine-2-thiolate (PyS) moieties in **2**, and finally two PyS ligands in **3**. This remarkable structural evidence reveals information that is pertinent to the transformation pathway of the reaction, i.e., from

Table 3
Selected bond distances and angles for $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**)

(a) Bond distances (Å)			
Os–C(1)	1.81(2)	Os–O(2)	2.11(2)
C(1)–O(1)	1.17(3)	Os–N(2)	2.21(5)
O(2)–N(1)	1.33(4)	Os–S(2)	2.38(1)
N(1)–C(2)	1.41(5)	Os–S(1)	2.41(1)
C(3)–C(4)	1.47(4)	S(1)–C(2)	1.93(2)
C(5)–C(6)	1.25(5)	N(1)–C(6)	1.39(5)
N(2)–C(8)	1.26(5)	C(2)–C(3)	1.39(3)
C(4)–C(5)	1.32(7)	S(2)–C(2′)	1.54(2)
N(2)–C(2′)	1.34(5)		
(b) Bond angles (°)			
C(1)–Os–N(2)	92.4(12)	C(1)–Os–O(2)	95.2(10)
C(1)–Os–S(1)	91.1(9)	C(1)–Os–S(2)	102.9(10)
C(2)–S(1)–Os	83.1(7)	O(2)–Os–S(1)	91.2(9)
O(2)–N(1)–C(6)	120(4)	N(1)–O(2)–Os	120(3)
C(6)–N(1)–C(2)	129(3)	O(2)–N(1)–C(2)	110(4)
C(3)–C(2)–S(1)	123(1)	C(3)–C(2)–N(1)	101(2)
C(2′)–S(2)–Os	93.2(9)	N(1)–C(2)–S(1)	135(2)
C(8)–N(2)–Os	134(4)	C(2′)–N(2)–Os	107(2)
N(2)–C(2′)–S(2)	101(3)		

pyridine-2-thione *N*-oxide to pyridine-2-thiolate, from triosmium cluster to monomeric osmium complex. These results prompted us to further explore the details of the reaction pathway using NMR and ESI-MS analytical methods.

2.2. Reaction of $Os_3(CO)_{12}$ with a controlled amount of 1-hydroxypyridine-2-thione and Me_3NO

The reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the presence of two equivalents of Me_3NO in CH_2Cl_2 at room temperature afforded complexes $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}SSC_5H_4N(O))$ (**4**, 44%) and $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SC_5H_4N(O))$ (**5**, 20%, Scheme 2). Products **4** and **5** were characterized by IR and ^1H NMR spectroscopy and the data are consistent with the reported values [8c]. Two trimethylamine-containing complexes $Os_3(CO)_{11}(NMe_3)$ or $Os_3(CO)_{10}(NMe_3)_2$ would be formed as intermediates through the activation of $Os_3(CO)_{12}$ by Me_3NO [15]. They then react readily with 1-hydroxypyridine-2-thione to give the triosmium complexes **4** and **5**.

2.3. In situ study of the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione by ^1H NMR spectroscopy

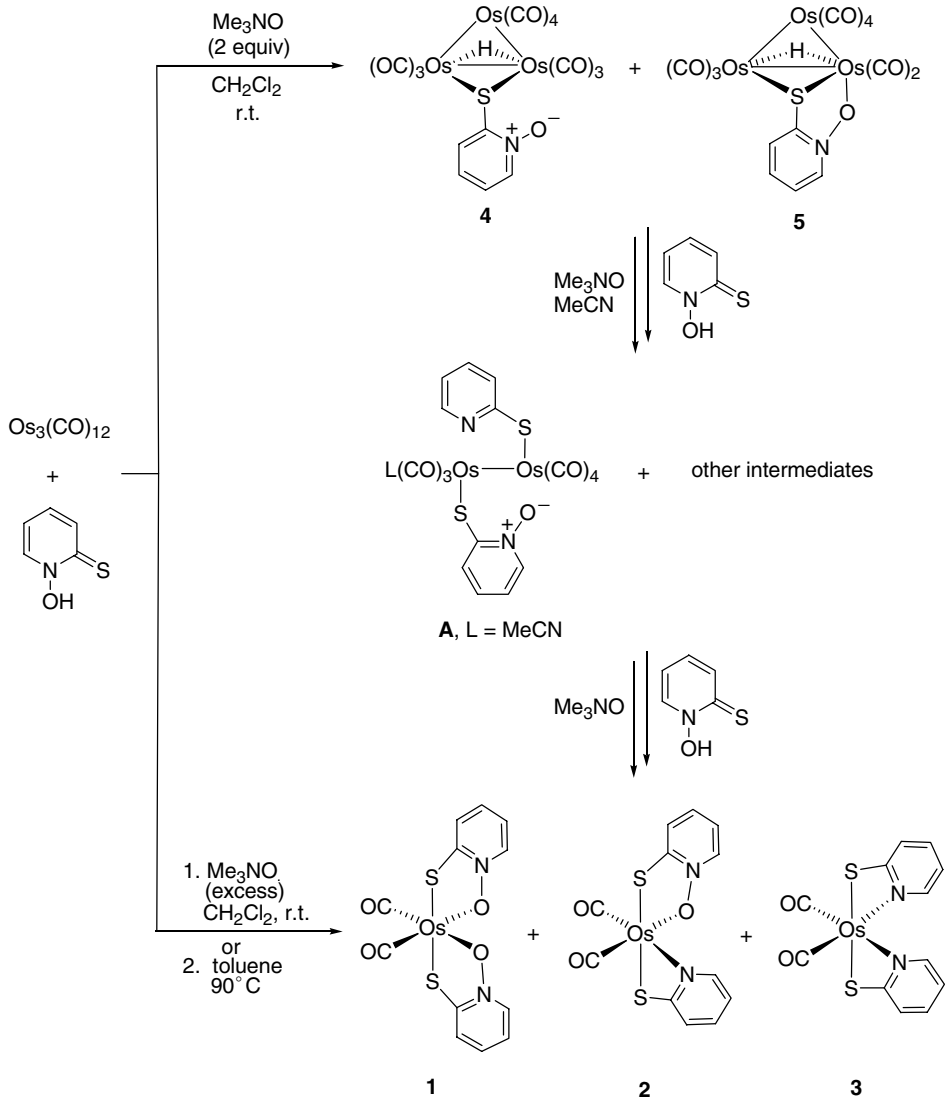
The reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the presence of Me_3NO was monitored by ^1H NMR spectrometry. Complexes **4** and **5** were found to be the reaction intermediates for the final products **1**–**3**. Several other intermediates were also detected with bridging hydrides that resonated between δ −14 and −17 ppm (δ −14.30, −15.26, −15.93 and −16.88 ppm) as well as two intermediates with terminal hydrides at δ −7.72 and −8.93 ppm. We believe that these peaks correspond to trinuclear and dinuclear osmium intermediates. During the reaction, the intensity of the bridging hydride peaks corresponding to **4**, **5** and other intermediates slowly decreased with the concomitant increase of peaks associated with the final products **1**–**3** as indicated by the ^1H NMR spectra. Because the reaction proceeded very rapidly at room temperature, we were unable to isolate and fully characterize the intermediates.

2.4. ESI-MS study: conversion of triosmium clusters into monomeric complexes

$Os_3(CO)_{12}$ can be activated by Me_3NO to form $Os_3(CO)_{11}(NMe_3)$ and $Os_3(CO)_{10}(NMe_3)_2$ [15]. The reactivities of these two slightly stabilized complexes are similar to that of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$. Therefore these two trimethylamine-containing complexes could react with 1-hydroxypyridine-2-thione to give $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}S\text{-}C_5H_4N(O))$ (**4**) and $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SC_5H_4N(O))$ (**5**). In the presence of an excess of Me_3NO, complexes **4** and **5** could react further with 1-hydroxypyridine-2-thione to give clusters in which each Os atom contains three CO ligands or less. The resulting complexes would then break down into dimeric and monomeric units. As a consequence, cluster complexes such as $Os_3H(PyOS)(PyOSH)(CO)_8$ and $Os_3H_2(PyOS)_2(CO)_7$ could be formed as intermediates by further substitution and oxidative addition reactions. This was corroborated by the results of the ^1H NMR study, during which several short-lived hydride peaks appeared.

Because most of the ν_{CO} absorptions for **4** and **5** were higher than 2000 cm^{-1}, the CO ligands were susceptible to nucleophilic attack by Me_3NO at room temperature. This would eliminate CO_2 molecules and create vacant sites to accommodate 1-hydroxypyridine-2-thione. As a consequence, a series of substitution and oxidative addition reaction occurred, leading to the formation of the final complexes **1**–**3**.

Although the application of ESI-MS to inorganic and organometallic chemistry has been limited, its soft nature is promising as a powerful tool for the analysis of fragile complexes [16]. This spectral technique enabled us to detect the unstable species that are generated in solution in the course of the chemical reaction [17]. We carried out an ESI-MS study to monitor the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the presence of excess Me_3NO at room temperature. Each spectrum was taken after reaction and dilution with acetonitrile (1:10) with an average of 10 consecutive scans. These *m*/*z* values assigned are for the most intensive peaks in each isotopic envelope. The mass spectrum exhibits isotope patterns that are characteristics of diosmium compounds (Fig. 3). The first set consists of peak at *m*/*z* 855.9 and peaks consistent with the sequential



Scheme 2.

loss of CO ligands (*m*/*z* 799.9, 772.0, and 744.1). The particularly intense peak at *m*/*z* 855.9 is assigned to the reaction intermediate of $[Os_2(CO)_7(NCMe)(\eta^1\text{-}SC_5H_4N(O))(\eta^1\text{-}SC_5H_4N)]$ (**A**), on the basis of its high-resolution isotope pattern in ESI-MS. Those peaks, corresponding to species by the loss of CO (*m*/*z* 28), may arise from either subsequent reaction intermediates or dissociation products of **A** in the gas phase. Similarly, the peak at *m*/*z* 839.9 may correspond to another set of reaction intermediate, singly charged protonated $[Os_2(CO)_7(NCMe)(\eta^1\text{-}SC_5H_4N)_2]$, accompanied by a series of sequential CO loss peaks at *m*/*z* 811.9, 783.9, 756.0, and 728.2. The conversion of triosmium compounds to dinuclear and mononuclear intermediates involves the ring opening of **4** and **5**. When excess Me_3NO is present, transformations occur by the sequential losses of CO and the binding of S, O, or N atoms from 1-hydroxypyridine-2-thione or pyridine-2-thione to the osmium metal centers, leading to the final products **1**–**3** (Fig. 2 in supplementary information). Note that products **1**–**3** were also observed under the same instrumental conditions. Furthermore, a peak at 522 is attributed to $[Os(pyS)_3]^+$ which suggests that the excess of amine oxide is leading to complete decarbonylation.

2.5. Transformation of pyridine-2-thione N-oxide to pyridine-2-thiolate

The monomeric complexes **1**–**3** could be generated by the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the absence of Me_3NO at 90 °C (Scheme 2). These results indicate that the pyridine-2-thione *N*-oxide ligand, a weaker oxidant than Me_3NO, was also able to promote the decarbonylation reaction. An intramolecular decarboxylation assisted by the *N*-oxide ligand most likely occurred during the reaction, for which the activation energy barrier was low and the reaction conditions were relatively mild. Therefore the coordinated CO

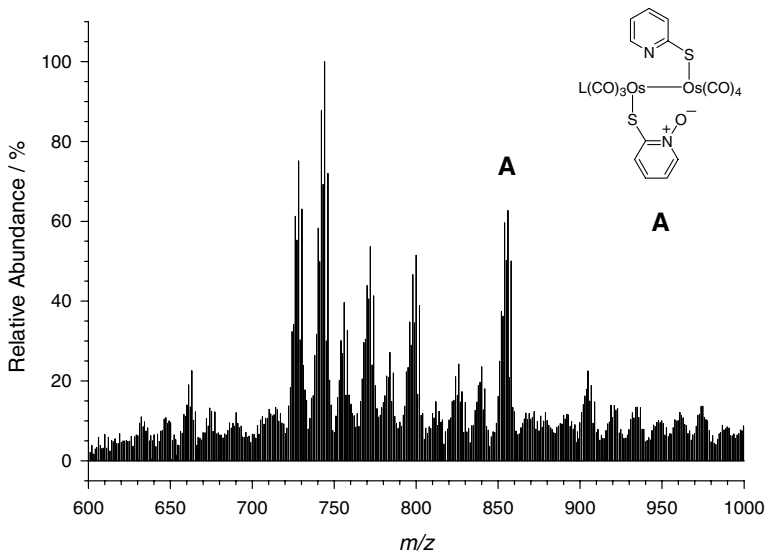


Fig. 3. ESI-mass spectrum of the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the presence of excess of Me_3NO. L = CH_3CN.

group can be oxidized and liberated while the pyridine-2-thione *N*-oxide is deoxygenated to form the pyridine-2-thiolate ligand.

In summary, the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione leads, not only to a stepwise conversion of the triosmium clusters into the monomeric osmium complexes, but also the concomitant transformation of the pyridine-2-thione *N*-oxide ligand into a pyridine-2-thiolate group. The structures of the final products **1**–**3** provide a hint for elucidating the reaction pathway, which was further supported by NMR and ESI-MS analyses.

3. Experimental

3.1. General data

Reagents were used as received. All manipulations, except for thin-layer chromatography (TLC), were performed under a nitrogen atmosphere by use of standard Schlenk techniques. Solvents were dried and distilled from sodium benzophenone ketyl or CaH_2 prior to use. Infrared spectra were recorded on a Perkin–Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Bruker ACP-300 FT-NMR spectrometer. FAB mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed by use of a Perkin–Elmer 2400 CHN elemental analyzer.

3.2. Reaction of $Os_3(CO)_{12}$ with excess 1-hydroxypyridine-2-thione and Me_3NO

To a solution of $Os_3(CO)_{12}$ (30 mg, 0.033 mmol) and 1-hydroxypyridine-2-thione (26 mg, 0.21 mmol) in CH_2Cl_2 (30 mL) was added a solution of Me_3NO (20 mg, 0.27 mmol) in CH_2Cl_2 (6.0 mL). The mixture was stirred at room temperature for 1.0 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel TLC plate (1-mm thickness) with hexane/CH_2Cl_2 (1:1) as the eluent to give $Os(CO)_2(\eta^2\text{-}SC_5H_4N)_2$ (**3**, 0.40 mg, 0.857×10^{-3} mmol, 1%) and $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**, 8.0 mg, 0.017 mmol, 17%). Continuous elution with a mixture of CH_2Cl_2 and hexane (2:1) gave $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**, 9.0 mg, 0.019 mmol, 19%) as yellow powder. For **1**: Anal. Calc. for $C_{12}H_8N_2O_4OsS_2$: C, 28.80; H, 1.61; N, 5.60. Found: C, 28.70; H, 1.56; N, 5.37%. IR (CH_2Cl_2): ν_{CO} = 2025 (vs), 1949 (vs) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.04 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H6), 7.69 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H3), 7.19 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H4), 6.79 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H5); ^{13}C NMR ($CDCl_3$): δ 179.8 (CO), 159.3 (C2), 138.2 (C6), 130.0 (C4), 128.4 (C3), and 117.6 (C5); MS (FAB, ^{192}Os): *m*/*z* 500 (M^+), 472 (M^+–CO), 444 (M^+–2CO). For **2**: IR (CH_2Cl_2): ν_{CO} = 2026 (vs), 1952 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.16 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H6(PyOS)), 7.80 (dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H6(PyS)), 7.68 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H3(PyOS)), 7.39 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H4(PyS)), 7.21 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H4(PyOS)), 6.82 (m, 1H, H5(PyOS)), 6.81 (m, 1H, H3(PyS)), 6.75 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H5(PyS)); ^{13}C NMR ($CDCl_3$): δ 182.0 (CO), 181.1 (CO), 176.5 (C2(PyS)), 159.0 (C2(PyOS)), 143.0 (C6(PyOS)), 138.3 (C6(PyS)), 137.2 (C4(PyS)), 130.3

(C4(PyOS)), 128.0 (C3(PyOS)), 127.9 (C3(PyS)), 117.9 (C5(PyS)), 117.1 (C5(PyOS)); MS (FAB, ^{192}Os): *m/z* 484 (M^+), 456 (M^+–CO), 428 (M^+–2CO).

3.3. Reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the presence of two equivalents of Me_3NO

To a solution of $Os_3(CO)_{12}$ (49 mg, 0.054 mmol) and 1-hydroxypyridine-2-thione (24 mg, 0.19 mmol) in CH_2Cl_2 (50 mL) was added a solution of Me_3NO (10 mg, 0.13 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature and monitored by IR for 2.0 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel TLC plate (1-mm thickness) with hexane/CH_2Cl_2 (1:1) as the eluent to give $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SC_5H_4N(O))$ (**5**, 10 mg, 0.011 mmol, 20%) and $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}S\text{-}C_5H_4N(O))$ (**4**, 23 mg, 0.024 mmol, 44%). For **4**: IR (CH_2Cl_2): ν_{CO} = 2111 (m), 2074 (vs), 2062 (s), 2024 (vs), 2003 (sh), 1986 (sh), and ν_{NO} = 1222 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.16 (d, $^3J_{HH}$ = 5.6 Hz, 1H, H6), 7.40 (d, $^3J_{HH}$ = 6.6 Hz, 1H, H3), 7.14–7.22 (m, 2H, H4 and H5), −17.49 ($^1J_{OsH}$ = 33.6 Hz, 1H, Os–H–Os). For **5**: IR (CH_2Cl_2): ν_{CO} = 2097 (m), 2056 (s), 2012 (s), 1998 (s), and 1928 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.44 (d, $^3J_{HH}$ = 6.4 Hz, 1H, H6), 8.05 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H3), 7.46 (t, $^3J_{HH}$ = 7.9 Hz, 1H, H4), 7.23 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H5), −14.55 (s, 1H, Os–H–Os).

3.4. Monitor of the reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione by ^{1}H NMR spectrometer

To a solution of $Os_3(CO)_{12}$ (29 mg, 0.032 mmol) and 1-hydroxypyridine-2-thione (26 mg, 0.21 mmol) in $CDCl_3$ (0.25 mL) was added a solution of Me_3NO (14 mg, 0.19 mmol) in $CDCl_3$ (0.25 mL). The mixture was monitored by ^{1}H NMR spectrometry. In addition to the complexes **4** and **5**, several bridging hydride peaks were observed at δ −14.30, −15.26, −15.93, −16.88 ppm, as well as terminal hydride peaks at δ −7.72 and −8.93 ppm. Additional Me_3NO (4.5 mg) in $CDCl_3$ (0.25 mL) was then added. The intensity of the bridging hydride peaks corresponding to **4**, **5** and other intermediates slowly decreased and peaks associated with complexes **1**–**3** were observed as the final products in a ratio of 1.3:1.7:1.0. An unidentified byproduct was also found in an amount comparable to complex **1**.

3.5. Reaction of $Os_3(CO)_{12}$ with 1-hydroxypyridine-2-thione in the absence of Me_3NO

1-Hydroxypyridine-2-thione (32 mg, 0.25 mmol) and $Os_3(CO)_{12}$ (23 mg, 0.025 mmol) were dissolved in toluene (20 mL). The mixture was then stirred at 90 °C for two days. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate (1-mm thickness) with hexane/CH_2Cl_2 (1:1) as the eluent to give $Os(CO)_2(\eta^2\text{-}SC_5H_4N)_2$ (**3**, 3.0 mg, 0.64×10^{-2} mmol, 1%) and $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))(\eta^2\text{-}SC_5H_4N)$ (**2**, 9.0 mg, 0.019 mmol, 25%), $Os(CO)_2(\eta^2\text{-}SC_5H_4N(O))_2$ (**1**, 5.0 mg, 0.010 mmol, 13%) and an unidentified complex (5.0 mg).

3.6. Electrospray ionization mass spectrometry

To a solution of $Os_3(CO)_{12}$ (20 mg, 0.022 mmol) and 1-hydroxypyridine-2-thione (17 mg, 0.13 mmol) in CH_2Cl_2 (30 mL) was added a solution of Me_3NO (5.0 mg, 0.067 mmol) in CH_2Cl_2 (10 mL). After stirring at room temperature for 30 min, 1.0 mL of the reaction mixture was taken, diluted with acetonitrile (10 mL), and then immediately subjected to ESI-Mass analysis.

All mass spectrometry experiments were performed on a Finnigan LCQ mass spectrometer (Thermo Finnigan, San Jose, CA, USA). The final sample solution was directly injected at 5.0 μL/min into the mass spectrometer and electrosprayed with a spray voltage of 4.25 keV. Spectra were collected in the positive ion mode. Each spectrum represents an average of 10–20 individual scans. Calibration of the mass range (50–2000) was carried out with a standard mixture of MRFA, caffeine, and Ultramark 1621.

3.7. Crystallographic structure determination

Crystals of **1** and **2** were grown from a mixture of CH_2Cl_2/*n*-hexane at −5 °C for X-ray diffraction studies. Suitable specimens were mounted in thin-walled glass capillaries and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Unit cell parameters were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data were collected by use of the $\omega/2\theta$ mode. The systematic absences in the diffraction data of **1** and **2** unambiguously established the space group as *C*2/*c*. All intensity data were corrected for Lorentz-polarization and absorption (empirical Ψ corrections). The structures of **1** and **2** were solved by use of the direct methods SHELX-97 and MULTAN, respectively [18,19]. All remaining non-hydrogen atoms were located from the difference Fourier maps, and were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement factors. The molecule **2** sits on a crystallographic twofold axis such that the five-membered *O,S*-chelate pyridine-2-thione *N*-oxide ring and the four-membered *N,S*-chelate pyridine-2-thiolate ring are disordered with respect to each other, the

disorder being 50/50 as required crystallographically. Calculations and full-matrix least-squares refinements were performed by using of the SHELX-97 and NRCVAX program package [18,20].

4. Supplementary material

ESI-Mass spectra. CCDC-221574 and -221575 contains the supplementary crystallographic data for this paper. Copies of this information may 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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