Reactions of 1-Hydroxypyridine-2-thione with Triosmium Clusters. Preparation and Transformation of *N*-Oxide-Containing Osmium Complexes

Jui-Te Hung,[†] Sudalaiandi Kumaresan,[†] Li-Chun Lin,[†] Yuh-Sheng Wen,[†] Ling-Kang Liu,[†] Kuang-Lieh Lu,*[,†] and Jih Ru Hwu*[,†,‡]

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Republic of China, and Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

Received March 6, 1996[⊗]

The reaction of 1-hydroxypyridine-2-thione with $Os_3(CO)_{11}(NCMe)$ has yielded three new complexes $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**1**, 11% yield), $Os_3(CO)_{10}(\mu\text{-H})(\eta^2\text{-S-}C_5H_4N(O))$ (**2**, 16% yield), and $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4N(O))$ (**3**, 3% yield). Similarly, treatment of complex $Os_3(CO)_{10}(NCMe)_2$ with this ligand has produced the major complexes **1** and trace of **3**. Prolonging the above two reactions increased the yield of **3**. Treatment of 1-hydroxypyridine-2-thione with triosmium isocyanide complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (**a**, R = CH_2-Ph; **b**, R = Pr) has led to the formation of $Os_3(CO)_9(\mu\text{-H})(CNR)(\eta^2\text{-}SC_5H_4N(O))$ (**4**), $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-C=NHCH}_2Ph)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**5**), and $Os_3(CO)_9(\mu\text{-H})(CNR)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**6**). The **4**:**5** ratio depended upon the nature of the alkyl groups of the coordinated isocyanide. Reaction of either **1** or **2** with Me_3NO resulted in CO loss and formation of complex **3**. Thermolysis of **1** at 80 °C generated $Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-pyS})$ (**7**), $Os_3(CO)_9(\mu\text{-OH})(\mu_3\text{-pyS})$ (**8**), and byproduct CO_2. Upon being heated at 80 °C, **3** was converted to **7** and **8** in a ratio of 1:4 as indicated by an in-situ NMR study. These observations show that **3** is an intermediate for the formation of **8** from **1**. Crystal structures of **1**, **4b**, **5a**, and **8** were determined by X-ray diffraction analyses. The overall results indicate that the *N*-oxide group in these complexes exhibits versatile bonding modes on triosmium clusters.

Introduction

Ligand 1-hydroxypyridine-2-thione can bond to one metal through its S and O atoms in a bidentate fashion, yet it can link two metals through its S atom in bridging mode.[1] In addition, 1-hydroxypyridine-2-thione possesses antifungal activity.[2] Some metallic complexes containing 1-hydroxypyridine-2-thione as a ligand were also found to be biologically active.[1] Little information, however, has been reported on the reactivities of 1-hydroxypyridine-2-thione with metal clusters. As a part of our research program into the properties of trimetal isocyanide clusters[3] and into the development of metal *N*-oxide complexes as DNA cleaving agents,[4] we have investigated the reactions of 1-hydroxybenzotriazole with osmium clusters.[5] Herein we report the reactions of 1-hydroxypyridine-2-thione with "lightly stabilized" complexes $Os_3(CO)_{11}(NCMe)$, $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{10}(CNR)(NCMe)$. In addition to the isolation of a variety of novel pyridinethione *N*-oxide-ligated triosmium clusters, interesting transformations of these new complexes were also observed.

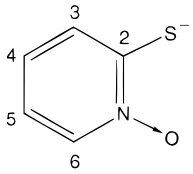


Figure 1. Numbering scheme for the NMR assignment.

Results

Reaction of $Os_3(CO)_{11}(NCMe)$ with 1-Hydroxypyridine-2-thione. Treatment of the "lightly stabilized" complex $Os_3(CO)_{11}(NCMe)$ with 1-hydroxypyridine-2-thione in CH_2Cl_2 afforded $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**1**, 11% yield), $Os_3(CO)_{10}(\mu\text{-H})(\eta^2\text{-S-}C_5H_4N(O))$ (**2**, 16% yield), and $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4N(O))$ (**3**, 3% yield, eq 1). Prolonging the reaction increased the yield of complex **3**. The formation of complex **1** was confirmed by IR, ^1H NMR, ^{13}C NMR, and mass spectra, as well as elemental and X-ray crystallographic analyses. The ^1H and ^{13}C NMR data for the complexed 1-hydroxypyridine-2-thione ligand follow the numbering system shown in Figure 1. The ^1H NMR spectrum of **1** showed a hydride signal at δ −17.49 ppm with satellites

[†] Academia Sinica.
[‡] National Tsing Hua University.
[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) (a) Manivannan, V.; Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 769. (b) Castano, M. V.; Sanchez, A.; Casas, J. S.; Sordo, J.; Brianso, J. L.; Pinielle. J. F.; Solans, X.; Germain, G.; Debaerdemaeker, T.; Glaser, J. *Organometallics* **1988**, *7*, 1897. (c) Davidson, J. L.; Preston, P. N.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1983**, 783. (d) Barnett, B. L.; Kretschmar, H. C.; Hartman, F. A. *Inorg. Chem.* **1977**, *16*, 1834.

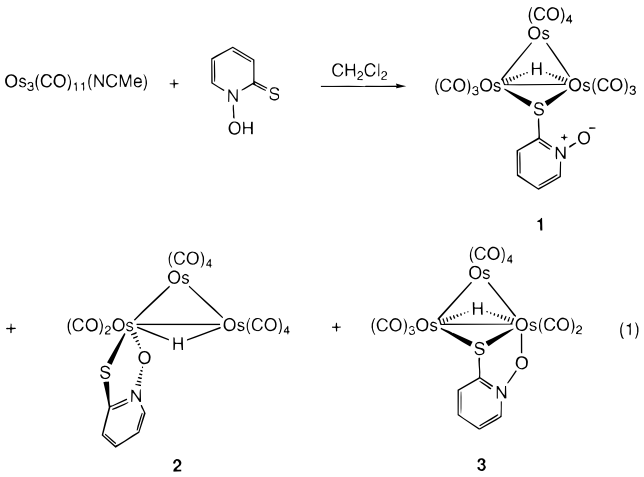
(2) Sijipesteijn, A. K.; Janssen, M. J. *Nature* **1958**, *182*, 1313.

(3) (a) Lu, K. L.; Liu. L. K.; Su, C. J.; Gau, H. M.; Wang, Y.; Lee, G. S. *J. Organomet. Chem.* **1994**, *482*, 67. (b) Lu, K. L.; Chung, M. L.; Lu, P. Y.; Gau, H. M.; Hong, F. E.; Wen, Y. S. *Organometallics* **1994**, *13*, 3177. (c) Lin, Y. W.; Gau, H. M.; Wen, Y. S.; Lu, K. L. *Organometallics* **1992**, *11*, 1445. (d) Lu, K. L.; Chen, C. J.; Lin, Y. W.; Gau, H. M.; Hong, F. E.; Wen, Y. S. *Organometallics* **1993**, *12*, 2188.

(4) (a) Nagai, K.; Carter, B. J.; Xu, J.; Hecht, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 5099. (b) Neyhart, G. A.; Cheng, C. C.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1463. (c) Cheng, C. C.; Goll, J. G.; Neyhart, G. A.; Welch, T. W.; Singh, P.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 2970. (d) Welch, T. W.; Neyhart, G. A.; Goll, J. G.; Ciftan, S. A.; Thorp, H. H. *J. Am. Chem. Soc.* **1993**, *115*, 9311.

(5) Lu, K. L.; Kumaresan, S.; Wen, Y. S.; Hwu, J. R. *Organometallics* **1994**, *13*, 3170.

S0276-7333(96)00176-8 CCC: $12.00

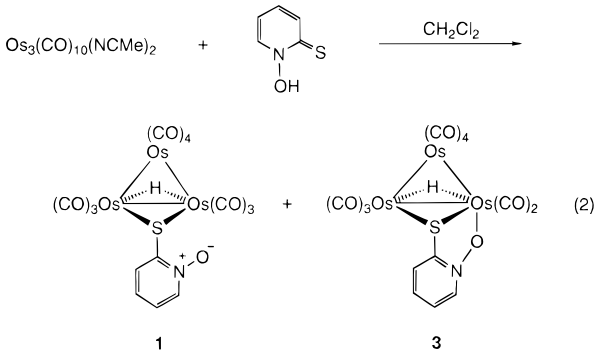


on both sides resulting from an $^{187}Os-H$ coupling with $^{1}J_{OsH} = 33.6$ Hz. We thus concluded that a doubly bridged, symmetrical triosmium complex was formed.[6] Furthermore, the chemical shifts of H3 and H6 for the complexed ligand showed resonances at δ 7.40 and 8.16 ppm, respectively. These two resonances compared well with those of its sodium salt[1d] (δ 7.44 and 8.10 ppm) and again suggested a thiolate coordination mode without *N*-oxide moiety participation. Surprisingly, the six CO resonances were almost identical with those of $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-R})$ (R = Et, Ph, and Py) reported by Lewis et al.[7] The presence of a noncoordinated *N*-oxide moiety was also indicated by the high polarity of the molecule, which was eluted with a highly polar solvent from a silica gel TLC plate. The IR spectrum of **1** exhibited a peak at 1222 cm^{-1}, which was attributed to the absorption of the uncoordinated N−O bond.[1a]

Through spectroscopic analyses, the pyridinethione ligand in complex **2** was found to coordinate through both the oxygen and the sulfur atoms on the same osmium. Its hydride resonance was greatly deshielded (δ −13.78 ppm) in comparison with that of the sulfur coordinated complex **1** (δ −17.49 ppm). This may be due to the inductive effect of the *N*-oxide moiety in **2**. Moreover, the resonances of the complexed ligand clearly showed an upfield shift for H6 (δ 7.81 ppm) and a downfield shift for H3 (δ 7.75 ppm) relative to **1**. The ^{13}C NMR spectrum of this complex showed 10 carbonyl resonances indicating an asymmetric structure. The five aromatic carbon resonances were found to be almost identical to those of the bidentate modes of complexes **4b** and $Zn(S\text{-}O\text{-}NC_5H_4)_2$,[1d] whose structures have been well characterized. The molecular ion peaks of **1** and **2** were found to be identical (*m*/*z* 983) in their FAB mass spectra.

The proton chemical shift for H3 and H6 of the complexed ligand in **3** showed two resonances at δ 8.05 and 8.44 ppm, respectively. These resonances were markedly different from those of both complexes **1** and **2**. Thus, we believe that a different coordination mode for the ligand exists in this complex. The nine carbonyl carbon resonances were observed in the ^{13}C NMR spectrum. These data suggest an asymmetrical structure as depicted in eq 1. The FAB mass spectrum of **3** also supports the assignment of the structure with a molecular ion peak at *m*/*z* 955 and peaks related to the subsequent loss of carbonyls.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-Hydroxypyridine-2-thione. We treated the "lightly stabilized" complex $Os_3(CO)_{10}(NCMe)_2$ with 1-hydroxypyridine-2-thione in CH_2Cl_2 at 0 °C to obtain complexes **1** (37% yield) and **3** (1% yield, eq 2). As in the case of $Os_3(CO)_{11}$(NCMe), the yield of **3** was found to be increased by prolonging the reaction. It is worth noting that the decarbonylation reaction occurred slowly under very mild conditions to afford **3** when complex **1** was stirred in CH_2Cl_2 at room temperature. In addition, compound **3** is believed to be a derivative from the reaction of **1** with residual Me_3NO in solution since its yield was increased when excess Me_3NO was used. It is of interest that complex **2** was not found in this reaction, whereas, in the case of $Os_3(CO)_{11}$(NCMe), complex **2** was the major product.



When complex $[Os_3(CO)_{10}(\mu\text{-H})(NCMe)_2][BF_4]$[8] was treated with 1-hydroxypyridine-2-thione sodium salt, only complex **1** and trace amounts of unidentified compounds were obtained after purification over a silica gel plate. This result indicates that the sulfur atom succeeds in coordinating to the osmium cluster considerably more often than the oxygen of the ligand does.

Molecular Structure of Complex 1. By use of single-crystal X-ray diffraction, the structure of complex **1** was obtained as shown in Figure 2. The crystallographic data as well as selected bond distances and angles are given in Tables 1−3. The three osmium atoms define a triangle with Os−Os distances ranging from 2.8511(7) to 2.8657(7) Å, which are slightly shorter than the average metal−metal bond distance of 2.877(3) Å found in $Os_3(CO)_{12}$.[9] The Os(2) and the Os(3) atoms are *edge*-bridged by the hydride (located and refined) and the S atom of the ligand. The average Os−S bond distance is 2.422(3) Å and the S−C(11) bond distance is 1.79(1) Å,[10] indicating that the deprotonated 1-hydroxypyridine-2-thione is coordinated in the thiolate form (3-electron donor) rather than thione. The N−O bond distance (1.32(1) Å) is close to the average N−O

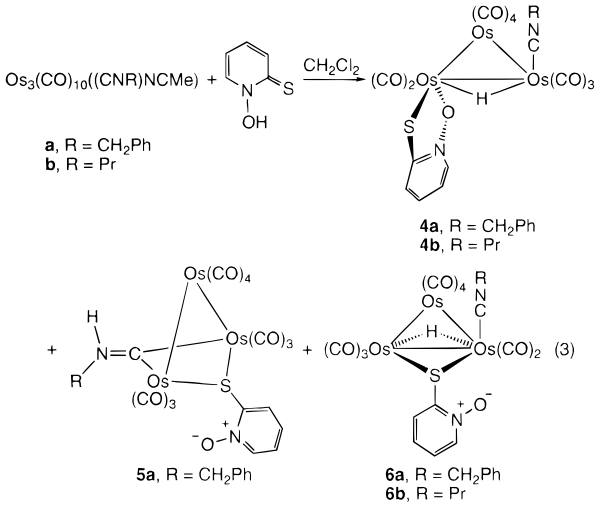
(6) Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain G. N.; Tayor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 754.
(7) (a) Brodie, A. M.; Holden, H. D. Lewis, J.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1986**, 633. (b) Bryan, E. G.; Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196.
(8) Anson, C. E.; Ditzel, E. J.; Fajardo, M.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2723.
(9) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(10) Ainscough, E. W.; Brodie, A. M.; Ingham, S. L.; Kotch, T. G.; Lees, A. J.; Lewis, J.; Waters, J. M. *J. Chem. Soc., Dalton Trans.* **1994**, 1.

Table 1. Crystal and Intensity Collection Data for Complexes 1, 4b, 5a, and 8

	complex			
	1	**4b**	**5a**	**8**
formula	$Os_3C_{15}H_5NO_{11}S$	$Os_3C_{18}H_{12}N_2O_{10}S$	$Os_3C_{23}H_{12}N_2O_{11}S$	$Os_3C_{14}H_5NO_{10}S$
fw	977.86	1018.96	1119.25	1899.71
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
cryst size (mm)	0.31 × 0.19 × 0.25	0.47 × 0.44 × 0.44	0.19 × 0.22 × 0.19	0.44 × 0.38 × 0.31
a, Å	8.1157(7)	9.2142(8)	12.040(2)	14.010(3)
b, Å	9.605(1)	9.5781(9)	17.668(2)	16.251(5)
c, Å	14.388(2)	14.4956(8)	28.408(3)	17.615(4)
α, deg	88.043(9)	74.537(6)		
β, deg	83.063(8)	85.963(6)	99.40(1)	102.50(2)
γ, deg	69.537(8)	79.158(7)		
V, Å^3	1043.0(2)	1210.7(2)	5961.9(14)	3915.5(16)
D (calc), g cm^{-3}	3.114	2.795	2.494	3.223
Z	2	2	4	4
temp	ambient	ambient	ambient	ambient
radiation (Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
2*θ* (max), deg	49.8	49.8	44.9	49.9
scan type	*θ*/2*θ*	*θ*/2*θ*	*θ*/2*θ*	*θ*/2*θ*
no. of measd data	3964	4511	8170	7183
no. of obsd data ($I \geq 2.5\sigma(I)$)	3300	3571	4735	4969
no. of refined params	281	308	738	523
R, R_w, %	3.5, 4.4	4.8, 5.9	4.2, 4.7	3.2, 3.7
GOF	2.53	2.81	1.64	1.48
min, max resid density, e Å^3	−2.780, 2.550	−2.690, 3.740	−1.720, 1.290	−1.550, 1.090

value (1.30(2) Å) of a typical noncoordinated *N*-oxide group,[11] in accord with the high polarity of the molecule.

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with 1-Hydroxypyridine-2-thione. The reaction of activated triosmium clusters $Os_3(CO)_{10}(CNR)(NCMe)$ (**a**, R = CH_2-Ph) with 1-hydroxypyridine-2-thione in CH_2Cl_2 at room temperature resulted in the formation of $Os_3(CO)_9$-(μ-H)($CNCH_2Ph$)(η^2-$SC_5H_4N(O)$) (**4a**), $Os_3(CO)_{10}(\mu$-η^1-C=$NHCH_2Ph$)(μ-η^1-S-$C_5H_4N(O)$) (**5a**), and $Os_3(CO)_9(\mu$-H)($CNCH_2Ph$)(μ-η^1-S-$C_5H_4N(O)$) (**6a**, eq 3). In contrast,



two products **4b** and **6b** were obtained when R = Pr. Complexes **4a**, **5a**, and **6a** were identified by spectroscopic means, and complexes **4b** and **5a** were further characterized by single-crystal X-ray structure analyses. Complexes **4a**,**b** exhibited hydride resonances at δ −13.39 and δ −13.44 ppm, respectively. These values were very close to that of **2**, in which the *N*-oxide moiety was engaged in bonding to osmium. The coordination of the oxygen atom of the *N*-oxide was also revealed by the use of a less polar solvent as the eluent in separation

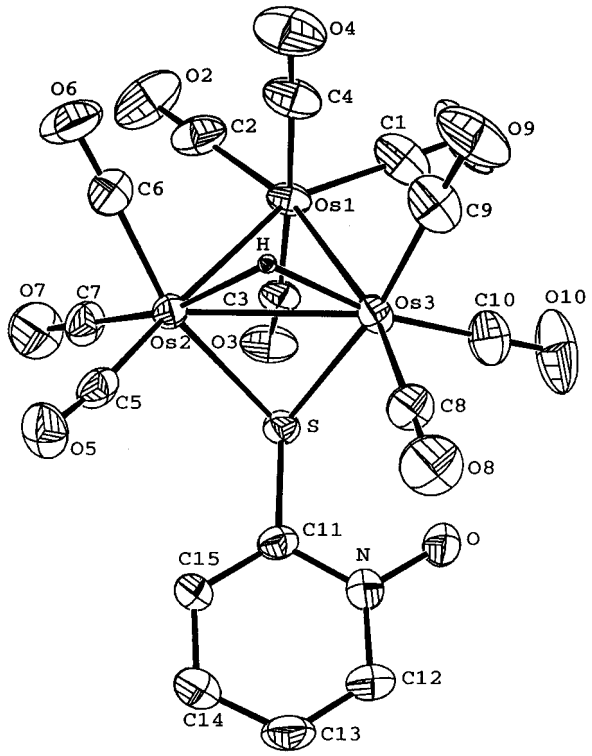


Figure 2. ORTEP diagram of $Os_3(CO)_{10}(\mu$-H)(μ-η^1-S-$C_5H_4N(O)$) (**1**).

by chromatography. In addition, the FAB mass spectra of **4a**,**b** showed their molecular ions at *m*/*z* 1072 and 1024, respectively, which correspond to the presence of nine carbonyls in the molecules. Further evidence for this was obtained from the ^{13}C NMR spectra. As compared to its sodium salt, the ^1H NMR spectra of the complexed ligand in **4a**,**b** displayed downfield shifts of H3 and upfield shifts of H6 (**4a**, δ 7.71 and 7.80 ppm; **4b**, δ 7.72 and 7.80 ppm). These observations indicate that the ligand is coordinated to the triosmium cluster through both the sulfur and the oxygen atoms. Upon complexation with the 1-hydroxypyridine-2-thione ligand, the proton signals of the propyl isocyanide ligands in **4**

(11) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, *S1*.

Table 2. Selected Bond Distances (Å) for Complexes 1, 4b, 5a, and 8 with Esd's in Parentheses

complex **1**		complex **4b**		complex **5a**		complex **8**	
Os(1)−Os(2)	2.8511(7)	Os(1)−Os(2)	2.9116(8)	Os(1)−Os(2)	2.883(1)	Os(1)−Os(2)	2.8090(9)
Os(1)−Os(3)	2.8658(7)	Os(1)−Os(3)	2.8393(8)	Os(1)−Os(3)	2.900(1)	Os(1)−Os(3)	3.202(1)
Os(2)−Os(3)	2.8576(6)	Os(2)−Os(3)	3.0646(8)	Os(2)−Os(3)	3.239(1)	Os(2)−Os(3)	2.8105(9)
Os(2)−S	2.433(3)	Os(3)−S	2.398(4)	Os(2)−S(1)	2.497(5)	Os(1)−S(1)	2.444(3)
Os(3)−S	2.410(3)	Os(3)−O	2.10(1)	Os(3)−S(1)	2.473(5)	Os(3)−S(1)	2.465(4)
Os(2)−C(6)	1.91(1)	S−C(14)	1.73(2)	Os(2)−C(21)	2.05(2)	Os(2)−N(1)	2.17(1)
Os(3)−C(9)	1.90(1)	N(1)−C(10)	1.17(3)	Os(3)−C(21)	2.09(2)	Os(1)−O(10)	2.152(9)
S−C(11)	1.79(1)	N(1)−C(11)	1.45(3)	S(1)−C(29)	1.82(2)	Os(3)−O(10)	2.133(9)
N−O	1.32(1)	N(2)−O	1.34(1)	N(1)−C(21)	1.30(2)	S(1)−C(11)	1.77(1)
N−C(11)	1.37(1)	N(2)−C(14)	1.36(2)	N(1)−C(22)	1.49(2)	N(1)−C(11)	1.36(2)
N−C(12)	1.35(2)	N(2)−C(18)	1.35(2)	N(2)−O(30)	1.31(2)	N(1)−C(15)	1.35(2)
C(11)−C(15)	1.37(2)	C(14)−C(15)	1.38(2)	N(2)−C(29)	1.36(2)	C(11)−C(12)	1.40(2)
C(12)−C(13)	1.34(2)	C(15)−C(16)	1.37(3)	N(2)−C(31)	1.34(3)	C(12)−C(13)	1.38(2)
C(14)−C(13)	1.36(2)	C(16)−C(17)	1.41(3)	C(29)−C(34)	1.36(3)	C(13)−C(14)	1.42(3)
C(14)−C(15)	1.38(2)	C(17)−C(18)	1.35(2)	C(31)−C(32)	1.37(3)	C(14)−C(15)	1.38(2)
Os(2)−C(7)	1.89(1)	Os(2)−C(10)	2.00(2)	C(32)−C(33)	1.31(3)	Os(1)−C(3)	1.88(2)
Os(3)−C(10)	1.91(1)	Os(3)−C(9)	1.81(2)	C(33)−C(34)	1.40(3)	Os(3)−C(8)	1.89(2)

Table 3. Selected Bond Angles (deg) for Complexes 1, 4b, 5a, and 8 with Esd's in Parentheses

complex **1**		complex **4b**		complex **5a**		complex **8**	
Os(1)−Os(2)−Os(3)	60.27(2)	Os(1)−Os(2)−Os(3)	56.66(2)	Os(1)−Os(2)−Os(3)	56.19(3)	Os(1)−Os(2)−Os(3)	69.47(2)
Os(1)−Os(3)−Os(2)	59.76(2)	Os(1)−Os(3)−Os(2)	58.95(2)	Os(1)−Os(3)−Os(2)	55.68(3)	Os(1)−Os(3)−Os(2)	55.24(2)
Os(3)−Os(1)−Os(2)	59.98(2)	Os(2)−Os(1)−Os(3)	64.39(2)	Os(2)−Os(1)−Os(3)	68.13(3)	Os(2)−Os(1)−Os(3)	55.29(2)
Os(1)−Os(2)−S	78.99(7)	Os(1)−Os(3)−O	87.7(2)	Os(1)−Os(2)−C(21)	78.1(6)	Os(3)−Os(2)−N(1)	84.4(3)
Os(1)−Os(3)−S	79.06(6)	Os(2)−Os(3)−O	85.8(3)	Os(2)−C(21)−Os(3)	102.9(8)	Os(2)−Os(1)−O(10)	84.6(2)
Os(2)−Os(3)−S	54.21(6)	Os(2)−C(10)−N(1)	175.9(14)	Os(1)−Os(3)−C(21)	77.2(6)	Os(2)−Os(3)−O(10)	84.9(3)
Os(2)−S−Os(3)	72.33(8)	N(1)−C(11)−C(12)	118.0(24)	Os(1)−Os(3)−S(1)	83.0(1)	Os(1)−S(1)−Os(3)	81.4(1)
Os(3)−Os(2)−S	53.46(6)	C(10)−N(1)−C(11)	174.7(18)	Os(1)−Os(2)−S(1)	83.0(1)	Os(2)−Os(1)−S(1)	79.12(8)
Os(3)−S−C(11)	110.2(4)	S−Os(3)−O	81.0(3)	Os(2)−S(1)−Os(3)	81.3(2)	Os(2)−Os(3)−S(1)	78.74(8)
Os(2)−S−C(11)	113.4(4)	Os(1)−Os(3)−S	165.2(1)	C(21)−N(1)−C(22)	130.1(16)	Os(1)−O(10)−Os(3)	96.7(3)
S−C(11)−N	115.3(8)	Os(2)−Os(3)−S	110.3(1)	Os(2)−S(1)−C(29)	107.1(6)	S(1)−Os(1)−O(10)	78.8(3)
C(11)−N−O	119.2(9)	Os(3)−O−N(2)	119.1(8)	Os(3)−S(1)−C(29)	108.5(6)	S(1)−Os(3)−O(10)	78.7(3)
C(12)−N−O	121.2(9)	Os(3)−S−C(14)	98.7(5)	C(29)−N(2)−O(30)	120.5(15)	Os(1)−Os(2)−N(1)	87.9(3)

undergo a slight upfield shift as compared to $Os_3(CO)_{11}$(CNPr). Accordingly, the complexes may be formulated as either $Os_3(CO)_9(\mu\text{-H})(CNR)(\eta^2\text{-S-}C_5H_4N(O))$ or $Os_3(CO)_9(\mu\text{-H})(CNR)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}SC_5H_4N(O))$.

Complex $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-C=NHCH}_2\text{Ph})(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**5a**) was characterized by IR, ^{1}H NMR, and mass spectra, as well as single-crystal X-ray diffraction measurements. Complex **5b** (R = CNPr) was not, however, isolated from the reaction. Complex **5a** did not show a hydride signal in the ^{1}H NMR spectrum. Instead, a broad peak was found at δ 11.43 ppm, which was attributed to the absorption of the NH of the bridging aminocarbyne group. In addition, the complexed ligand exhibited an upfield shift for H6 (δ 8.24 ppm *vs* 7.80 ppm in **4**). The high polarity of this compound suggested that the *N*-oxide moiety was not bound to an osmium atom. Therefore we concluded that the deprotonated 1-hydroxypyridine-2-thione ligand in **5a** was coordinated through the bridging sulfur atom. Our identification was further supported by the X-ray analysis.

Complex $Os_3(CO)_9(\mu\text{-H})(CNR)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**6**) exhibited different spectroscopic data from those of **5**, except that the polarity was similar. The infrared spectrum of **6a** showed the ν_{CN} absorption at 2196 cm^{-1}, characteristic of a terminally coordinated isocyanide ligand. Complex **6** displayed two hydride peaks (**6a**, δ −17.08 and −17.06 ppm in a ratio of 0.7:1; **6b**, −17.19, and −16.82 ppm in a ratio of 1:1). These may be attributed to the two positional isomers with different environments for the bridging hydride lignads, in which the isocyanide ligand may occupy the axial sites of different osmium atoms. The MS (FAB) spectrum of **6a** exhibited the molecular ion at *m*/*z* 1072 as well as the CO-loss fragmentation. The deprotonated 1-hydroxypyrdine-2-thione is proposed to coordinate to two osmium atoms in a bridging thiolate form without *N*-oxide coordination as indicated by its high polarity. Further evidence for the noncoordinated oxygen came from the ^{1}H NMR spectra for the complexed ligand. The chemical shifts for H6 (δ 8.18 in **6a**; δ 8.10 and 8.12 in **6b**) compared well to those of **1** (δ 8.16 ppm) and 1-hydroxypyrdine-2-thione sodium salt (δ 8.10 ppm), in which the oxygen was not involved in complexation. Attempts to obtain the single-crystal structure of **6** were unsuccessful.

Molecular Structures of 4b and 5a. Thermal ellipsoid diagrams of these two compounds are shown in Figures 3 and 4, respectively. Crystallographic data are listed in Table 1, while selected bond distances and angles are given in Tables 2 and 3. In the molecular structure of **4b**, the three osmium atoms define a triangle with the Os(2)−Os(3) distance of 3.0646(8) Å, which is typical of a hydride bridged Os−Os single bond.[12] The Os(3) center is chelated by the 1-hydroxypyridine-2-thione ligand via both sulfur and oxygen atoms, with sulfur in an equatorial and oxygen in an axial position. The isocyanide ligand occupies Os(2) in the axial position opposite to the *N*-oxide moiety. The bond angle around isocyanide nitrogen [C(10)−N−C(11)] is 174.7(18)°, which is close to the value for the terminal isocyanide ligands in $Fe_2(CNEt)_9$.[13] The electron-donating propyl group reduces the π-back-bonding capability from the metal to the C−N π*-orbital and preserves the linearity of the C(10)−N−C(11) group.[14] However, the propyl group is slightly disordered in the crystal (see Figure 3). The S−C(14) bond length of

(12) Deeming, A. J. *Adv. Organomet. Chem*. **1986**, *26*, 1.
(13) Bassett, J. M.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton. Trans*. **1981**, 219.
(14) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Wadsworth, Inc.: Belmont, CA 1985; Chapter 3.

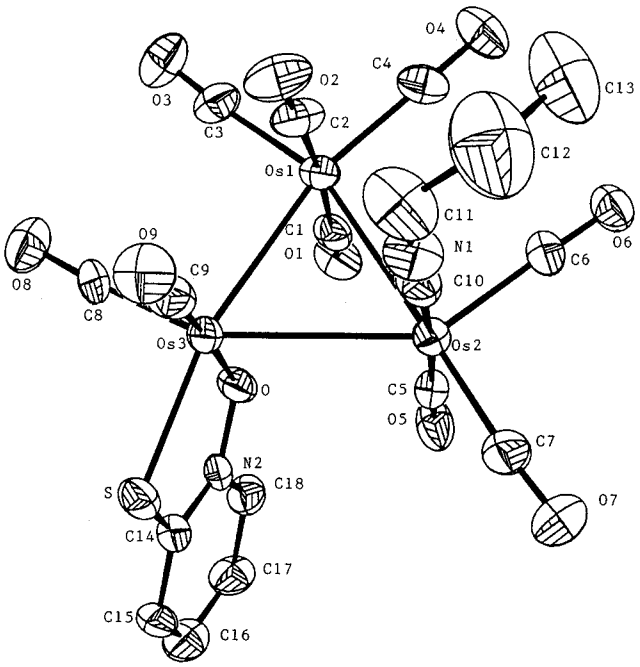


Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu\text{-H})(CNPr)(\eta^2\text{-}SC_5H_4N(O))$ (**4b**).

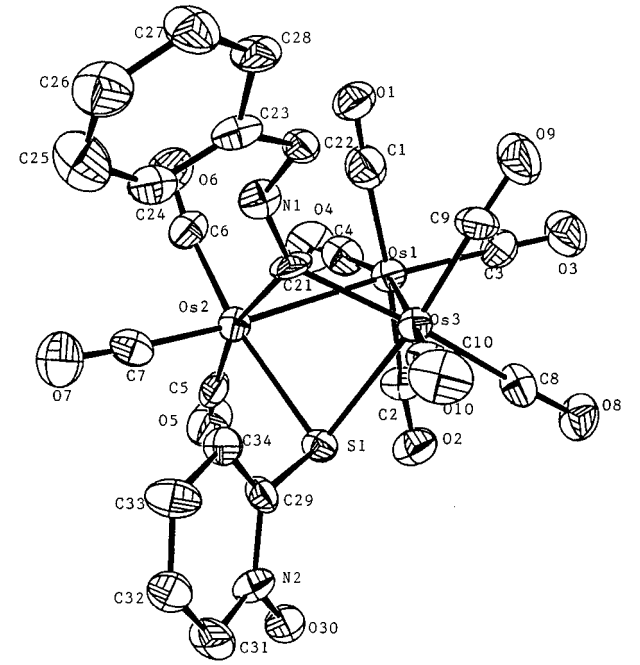
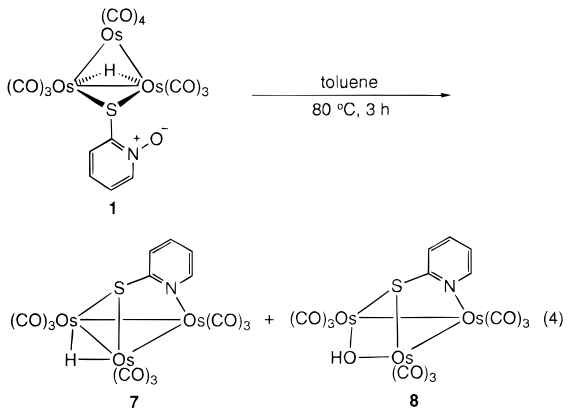


Figure 4. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}C{=}NHCH_2Ph)(\mu\text{-}\eta^1\text{-}S\text{-}C_5H_4N(O))$ (**5a**).

1.73(2) Å is shorter than that in complex **1** [1.79(1) Å] and those of bridging sulfido compounds,[7,8] but it is close to that of the thione form found in monometal complexes.[1b]

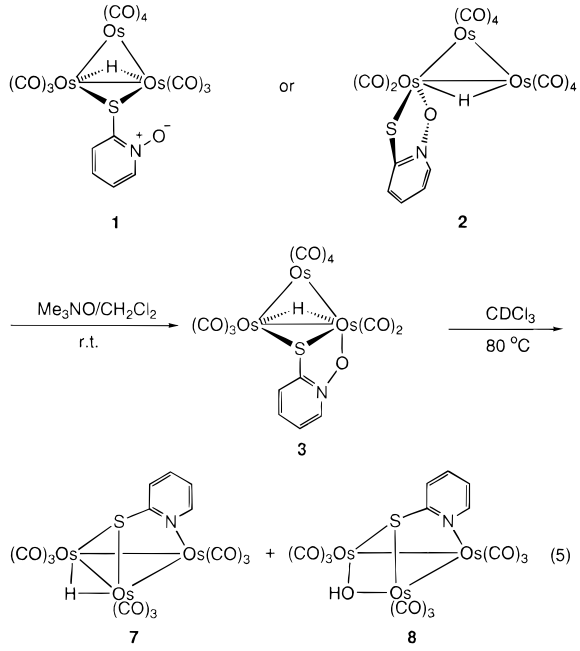
The structure of **5a** shown in Figure 4 exhibits a doubly bridged coordination both by sulfido and by aminocarbyne ligands. The Os(2)−Os(3) (3.239(1) Å) contact is considered to be nonbonding. The bond distances between the bridging sulfur atom and osmiums are 2.479 (5) and 2.473(5) Å, respectively. The bond angle of aminocarbyne C(21)−N(1)−C(22) is 130.1(16)°, which is similar to those in $Os_3(CO)_{10}(\mu\text{-}CONHPr^i)(\mu\text{-}C{=}NHCH_2Ph)$[2c,2d] and in $Os_3(CO)_{10}(\mu\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu\text{-}\eta^1\text{-}C{=}NHCH_2Ph)$.[4]

Thermolysis of Complex 1. Thermolysis of complex **1** in toluene at 80 °C afforded $Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-pyS})$ (**7**) and $Os_3(CO)_9(\mu\text{-OH})(\mu\text{-pyS})$ (**8**) (eq 4). The



carbon dioxide byproduct of this reaction was identified by GC/MS. Neither **7** nor **8** showed an absorption near 2100 cm^{-1}; thus, coordination is believed to occur on the third osmium atom.[15] Complex **7** exhibited identical spectral data to those obtained by others.[15] The nonhydrido complex **8** did not exhibit any peak related to the terminal or bridging hydride. Instead, a broad peak at δ −1.49 ppm appeared for the hydroxyl proton.[16] The complexed ligand in **8** also exhibited a similar chemical shift in comparison with those of **7**. Thus a μ_3-coordination existed, which was consistent with our IR observations.

Transformation of Complexes 1−3. Treatment of complex **1** with a 2-fold excess of trimethylamine *N*-oxide in CH_2Cl_2 at room temperature gave the complex $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4N(O))$ (**3**) in 76% yield (eq 5). In addition, a minor unidentified complex with a



(15) Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1982**, *233*, C55.

(16) (a) Hodge, S. R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, *931*. 15. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (c) Deeming, A. J.; Manning, P. J.; Rothwell, I. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1984**, 2039.

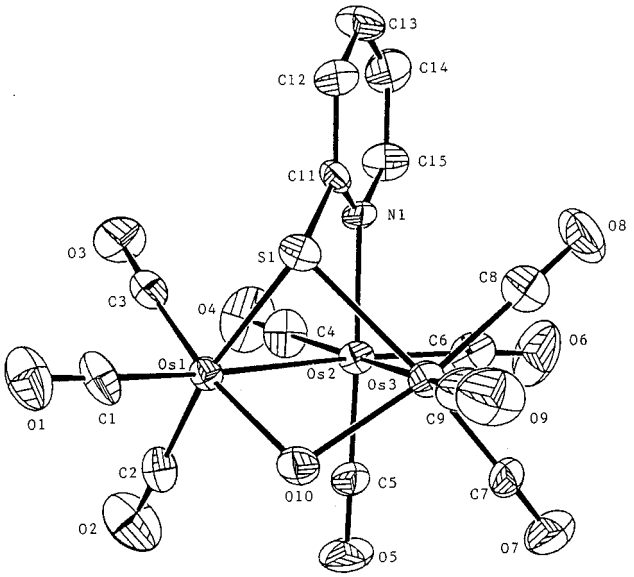


Figure 5. ORTEP diagram of $Os_3(CO)_9(\mu\text{-OH})(\mu\text{-pyS})$ (**8**).

hydride peak at δ −14.14 ppm was also observed. Attempts to characterize this compound were not successful. Treatment of **2** under similar conditions also afforded **3** in 51% yield. Upon being heated at 80 °C in $CDCl_3$ in a sealed NMR tube, complex **3** was converted to the major product **8** and the minor compound **7** in a ratio of 4:1 as well as several minor unidentified complexes.

Molecular Structure of Complex 8. The structure of complex $Os_3(CO)_9(\mu\text{-OH})(\mu_3\text{-pyS})$ was determined by single-crystal X-ray diffraction analysis. An ORTEP diagram of molecule **8** is shown in Figure 5. General data and collection procedures are listed in Table 1, and selected bond distances and angles are given in Tables 2 and 3. The three Os atoms define an isosceles triangle, in which the Os(1) and the Os(3) atoms are bridged by the S atom of the pyridine-2-thiolato ligand and also by the oxygen atom of the hydroxyl group. The doubly bridged Os(1)−Os(3) vector (3.2017(9) Å) is longer than the nonbridged bonds Os(1)−Os(2) (2.8104(9) Å) and Os(2)−Os(3) (2.8088(8) Å) and is considered to be nonbonding. The thioamide ligand, derived from the deoxygenation process, is coordinated to one face of the Os cluster via both the bridging sulfur and the nitrogen atoms. The hydroxyl proton was not located crystallographically. The average bond distance between bridging oxygen atom and two osmiums is 2.143(9) Å, which is very close to the reported bridging Os−O−Os distances.[16a,17]

Discussion

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with the 1-hydroxypyridine-2-thione ligand produced complex **1** as the main product. The generation of **1** is believed to be achieved via protonation of the activated metal cluster followed by substitution with a pyridinethione anion. In addition to **1**, complex **3** was formed as a minor product. Its formation can be explained in terms of further decarbonylation of complex **1** by intramolecular nucleophilic attack of the *N*-oxide moiety at the *bridged* osmium atom. The decarbonylation process takes place under very mild conditions. At room temperature complex **3** was found to be slowly formed when **1** was stirred in a solution of CH_2Cl_2. Similar results were obtained upon treatment of **1** with Me_3NO.

It is interesting to compare the reactivities of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ toward 1-hydroxypyridine-2-thione. In the case of $Os_3(CO)_{11}(NCMe)$, initial protonation followed by substitution with the sulfur atom of a pyridinethione anion may produce an intermediate of the form $Os_3(CO)_{11}(\mu\text{-H})(\eta^1\text{-S-}C_5H_4N(O))$ with a terminally coordinated thiolato ligand. As a consequence, the noncoordinated oxygen atom may replace a carbonyl group on the sulfur-coordinated osmium to give the bidentate five-membered ring complex **2**. This decarbonylation process may proceed through an alternative pathway to afford complex **1**, in which the coordinated sulfur replaces another carbonyl group on the adjacent $Os(CO)_4$ unit. In the case of $Os_3(CO)_{10}(NCMe)_2$, the plausible intermediate would be formulated as $Os_3(CO)_{10}(\mu\text{-H})(NCMe)(\eta^1\text{-S-}C_5H_4N(O))$, in which the labile acetonitrile group on the adjacent osmium center rather than CO ligands would be preferentially replaced by the coordinated sulfur atom of the ligand to form **1**. Consequently, formation of complex **2** was not observed when starting with $Os_3(CO)_{10}(NCMe)_2$. Once the complexes **1** and **2** were formed in the above two reactions, they underwent further decarbonylation by substitution of a CO ligand with the noncoordinated *N*-oxide moiety (complex **1**) or with the coordinated sulfur atom (complex **2**) to give complex **3**.

In the presence of a coordinated isocyanide ligand, the reaction of complex $Os_3(CO)_{10}(CNR)(NCMe)$ with 1-hydroxypyridine-2-thione exhibits two features that distinguish it from those of complexes $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$. First, the formation of products **4** and **6** shows that similar reaction pathways exist for reaction of these three osmium clusters with the ligand. Nevertheless, the lack of an analogue of **3** formulated as $Os_3(CO)_8(\mu\text{-H})(CNR)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4(O))$ indicated that the coordinated isocyanide ligand strengthens the Os−CO bonds and renders further decarbonylation of **4** and **6** difficult. Also, the isocyanide ligand can react with a proton to form a bridging aminocarbyne moiety. The ratio of the aminocarbyne product to the hydrido complexes depended upon the nature of the alkyl groups of the isocyanide. In the case of propyl isocyanide, the formation of complex **5b** was not observed. This maybe due to the weaker π-back-bonding in the propyl isocyanide, which prevents it from bridging two osmium atoms. On the other hand, the stronger π-back-bonding in the benzyl isocyanide could do this without difficulty.

It is worth noting that the transformation of **1** or **2** to complex **7** could be achieved at 80 °C. The presence of carbon dioxide as a byproduct indicates that an intramolecular *N*-oxide-assisted decarboxylation probably occurs during the reaction, for which the activation energy barrier is low and the reaction conditions are relatively mild. Decarbonylation processes at the third osmium atom in triosmium cluster often require much higher temperatures[15] or irradiation.[10] For example, the complex $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-py})$[7] yielded face-capped substitution products after attack by nitrogen on the third osmium at 110 °C.

Thermolysis of **1** could facilitate the interaction of the *N*-oxide moiety with an Os center and thus induce the

(17) Deeming, A. J.; Owen, D. W.; Powell, N. I. *J. Organomet. Chem.* **1990**, *398*, 299.

formation of **8**. Complex **3** is found to be the intermediate of this reaction. We propose that the transformation of **3** to **8** proceeds by the insertion of hydride into the N−O bond of the complexed ligand.[18] This results in the formation of a terminal Os−OH intermediate that possesses a tendency to undergo migration into the Os−Os metal bond, thereby forming a bridging μ-η^1-OH moiety.[18]

Experimental Section

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 over Na/benzophenone (for tetrahydrofuran and ether) or CaH_2 (for hexanes and CH_2Cl_2) and were freshly distilled before use. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. Mass spectra were recorded on a VG 70-250S mass spectrometer. GC/MS spectra were obtained on a Fisons MD800/GC8000 mass spectrometer. Elemental analyses were performed by use of a Perkin-Elmer 2400 CHN elemental analyzer.

Reaction of $Os_3(CO)_{11}(NCMe)$ with 1-Hydroxypyridine-2-thione. To a solution of $Os_3(CO)_{12}$ (194 mg, 0.214 mmol) in CH_2Cl_2 (150 mL) and MeCN (5 mL) was added a solution of Me_3NO (15 mg, 0.200 mmol) in a mixture of MeCN and CH_2Cl_2 (1:5, 6 mL). The mixture was stirred at room temperature for 1 h and filtered through a short column of silica gel. The solvent was removed under vacuum, and the resultant solid, $Os_3(CO)_{11}(NCMe)$, was redissolved in CH_2Cl_2 (300 mL) and cooled in an ice bath. A solution of 1-hydroxypyridine-2-thione (25 mg, 0.197 mmol) in CH_2Cl_2 (10 mL) was added slowly for 5 min to the above mixture. The ice bath was removed and stirring was continued for 1 h. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 and filtered to remove unreacted $Os_3(CO)_{12}$ (24 mg, 12%). The filtrate was concentrated and chromatographed on a silica gel TLC plate (4-mm thickness) with hexane/CH_2Cl_2 (1:1) as the eluent to give $Os_3(CO)_{10}(\mu\text{-H})(\eta^2\text{-S-}C_5H_4N(O))$ (**2**, 33 mg, 0.034 mmol, 16% yield) and $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4N(O))$ (**3**, 7 mg, 0.007 mmol, 3% yield). Continued elution with a mixture of CH_2Cl_2 and THF (9:1) afforded $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**1**, 22 mg, 0.023 mmol) in 11% yield as yellow powder. Data for **1**: 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, 1 H, $^3J_{HH}$ = 5.6 Hz, H6), 7.40 (d, 1 H, $^3J_{HH}$ = 6.6 Hz, H3), 7.14−7.22 (m, 2 H, H4 and H5), −17.49 (1 H, $^1J_{OsH}$ = 33.6 Hz, Os−H−Os); ^{13}C NMR ($CDCl_3$) δ 180.3, 179.7, 175.8, 173.6, 170.1, 169.0 (6 CO), 155.0 (C2), 140.1, 127.5, 124.9, and 124.8 (aromatic); MS (FAB, ^{192}Os) *m*/*z* 983 (M^+), 955 (M^+ − CO), 927 (M^+ − 2CO), 899 (M^+ − 3CO), 871 (M^+ − 4CO). Anal. Calcd for $C_{15}H_5NO_{11}Os_3S$: C, 18.42; H, 0.51; N, 1.43. Found: C, 18.48; H, 0.61; N, 1.25. Data for **2**: IR (CH_2Cl_2) ν_{CO} = 2130 (w), 2076 (s), 2049 (vs), 2013 (m), 2001 (m), 1977(w), 1926 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, $^3J_{HH}$ = 6.5 Hz, 1 H, H6), 7.75 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, H3), 7.17 (dt, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H4), 6.70 (dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H5), −13.78 (1 H, μ-H); ^{13}C NMR ($CDCl_3$): δ 158.9 (C2), 117.2 (C3), 130.6 (C4), 127.2 (C5), 137.9 (C6), 165.5, 166.7, 172.6, 173.3, 175.5, 176.3, 180.9, 181.5, 182.6, 189.8 (10 CO); MS (FAB, ^{192}Os) *m*/*z* 983 (M^+), 955 (M^+ − CO), 927 (M^+ − 2CO), 899 (M^+ − 3CO), 871 (M^+ − 4CO). Data for **3**: 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, *J* = 6.4 Hz, 1 H, H6), 8.05 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H3), 7.46 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, H4), 7.23 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H5), −14.55 (s, 1 H, μ-H); ^{13}C NMR ($CDCl_3$) δ 159.7 (C2), 124.3 (C3), 131.2 (C4 or C5), 129.3 (C5 or C4), 139.7 (C6), 168.8, 171.2, 172.6, 173.8, 176.2, 176.7, 179.7, 182.1, 187.5 (9 CO); MS (FAB, ^{192}Os) *m*/*z* 955 (M^+), 927 (M^+ − CO), 899 (M^+ − 2CO), 871 (M^+ − 3CO), 843 (M^+ − 4CO).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-Hydroxypyridine-2-thione. Method A. To a solution of $Os_3(CO)_{12}$ (81 mg, 0.089 mmol) in CH_2Cl_2 (80 mL) and MeCN (2 mL) was added a solution of Me_3NO (21 mg, 0.280 mmol) in a mixture of MeCN and CH_2Cl_2 (1:5, 15 mL). The mixture was stirred at room temperature for 1 h and filtered through a short column of silica gel. The solvent was removed under vacuum, and the resultant solid, $Os_3(CO)_{10}(NCMe)_2$, was redissolved in CH_2Cl_2 (80 mL) and cooled in an ice bath. A solution of 1-hydroxypyridine-2-thione (13 mg, 0.102 mmol) in CH_2Cl_2 (10 mL) was added slowly for 5 min to the above mixture. The ice bath was removed, and stirring was continued for 1 h. 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 the minor product $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-}SC_5H_4N(O))$ (**3**, 1 mg, 0.001 mmol, 1% yield). Continued elution with a mixture of CH_2Cl_2 and THF (9:1) as eluent afforded $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-}SC_5H_4N(O))$ (**1**, 32 mg, 0.033 mmol, 37% yield) as a yellow powder.

Method B. To a solution of $Os_3(CO)_{12}$ (200 mg, 0.221 mmol) in CH_2Cl_2 (100 mL) and MeCN (3.0 mL) was added a solution of Me_3NO (50 mg, 0.667 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 1 h and filtered through a column of silica gel. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 (100 mL) and cooled in an ice bath. A solution of $HBF_4{\cdot}Et_2O$ (54% by weight, 40 μL, 0.290 mmol) was injected to the above mixture and stirred for 10 min at 0 °C and 20 min at room temperature.[10] The solvent was removed under vacuum, and the residue was redissolved in CH_2Cl_2 (100 mL). This was followed by the addition of 1-hydroxylpyridine-2-thione sodium salt in dried acetone (5.0 mL) at room temperature for 2 h. Removal of the solvent and chromatography on a silica gel TLC plate (2-mm thickness) with CH_2Cl_2/THF (2:1) as eluent gave complex **1** (49 mg) in 23% yield.

Reaction of $Os_3(CO)_{10}(NCMe)(CNCH_2Ph)$ with 1-Hydroxypyridine-2-thione. To a solution of $Os_3(CO)_{11}(CNCH_2Ph)$ (346 mg, 0.348 mmol) in CH_2Cl_2 (250 mL) and MeCN (3.0 mL) was added a solution of Me_3NO (30 mg, 0.400 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 0.5 h and filtered through a short pad of silica gel. The solvent was removed under vacuum and the resultant yellow residue dissolved in CH_2Cl_2 (200 mL). A solution of 1-hydroxypyridine-2-thione (56 mg, 0.441 mmol) in 10 mL of CH_2Cl_2 was then introduced to the above stirring solution for a period of 30 min and allowed to react for another 3 h at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel plate (2-mm thickness) with 3:1 of hexane/CH_2Cl_2 as eluent to afford $Os_3(CO)_9(\mu\text{-H})(CNCH_2Ph)(\eta^2\text{-}SC_5H_4N(O))$ (**4a**; 27 mg, 0.026 mmol) in 7% yield. ^{1}H NMR ($CDCl_3$) δ −13.39 (s, 1 H, μ-H), 5.13 (AA′, 2 H, $CNCH_2$), 7.80 (d, 1 H, $^3J_{HH}$ = 6.9 Hz, H6), 7.71 (d, 1 H, $^3J_{HH}$ = 8.7 Hz, H3), 7.11 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, H4), 6.64 (t, 1 H, $^3J_{HH}$ = 6.6 Hz, H5) 7.24−7.41 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 49.3 ($CNCH_2$), 159.1 (C2), 116.8 (C3), 130.1 (C4), 127.0 (C5), 138.0 (C6), 168.1 170.1, 173.8, 174.7, 177.8, 181.7, 182.6, 184.6, and 185.4 (9 CO); IR (CH_2Cl_2) ν_{CN} = 2223 (m), ν_{CO} = 2092 (m), 2060 (s), 2027 (s), 2001 (s), and 1914 (m) cm^{-1}; MS (FAB, ^{192}Os) *m*/*z* 1072 (M^+). Anal. Calcd for $Os_3C_{22}H_{12}N_2O_{10}S$: C, 24.76; H, 1.13; N, 2.63. Found: C, 25.16; H, 1.34; N, 2.53. Continued elution with 1:20 THF/CH_2Cl_2 gave complexes $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-C=NHCH}_2Ph)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**5a**, 38 mg, 0.035 mmol) and $Os_3(CO)_9(\mu\text{-H})(CNCH_2Ph)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**6a**, 29 mg, 0.027 mmol) in 10% and 8% yields, respectively. Complex **5a**: ^{1}H NMR (acetone-d_6) δ 11.43 (bs, 1 H, NH), 4.83 (m, 2 H, $CNCH_2$), 8.24 (d, 1 H, $^3J_{HH}$ = 6.4 Hz, H6), 7.85 (d, 1 H, $^3J_{HH}$ = 7.5 Hz, H3), 7.29−7.50 (m, 7 H;

(18) Frauenhoff. G. R. *Coord. Chem. Rev.* **1992**, *121*, 131.

Ph, H4 and H5); IR (CH_2Cl_2) ν_{CO} = 2099 (m), 2064 (s), 2048 (m), 2013 (vs), 1990 (m), and 1230(w) cm^{-1}, MS (FAB, ^{192}Os) *m/z* 1100 (M^+), 960 ($M^+ - 5CO$). Anal. Calcd for $Os_3C_{23}H_{12}N_2O_{11}S$: C, 25.19; H, 1.19; N, 2.56. Found: C, 25.49; H, 1.16; N, 2.51. Complex **6a**: IR (CH_2Cl_2) ν_{CN} = 2196 (m), ν_{CO} = 2084 (m), 2060 (vs), 2034 (s), 2006 (s), and 1998 (sh) cm^{-1}. Anal. Calcd for $Os_3C_{23}H_{12}N_2O_{11}S$: C, 24.76; H, 1.13; N, 2.63. Found: C, 25.27; H, 1.11; N, 2.49. ^1H NMR (acetone-d_6): δ −17.08 and −17.06 (s, 1 H, μ-H, two isomers in a ratio of 0.7:1), 5.42 and 5.39 (s, 2 H, $CNCH_2$, two isomers in a ratio of 0.7:1), 8.18 (m, 1 H, $^3J_{HH}$ = 6.5 Hz, H6), 7.64 (m, 1 H, $^3J_{HH}$ = 7.5 Hz, H3), 7.23−7.58 (m, 7 H; Ph, H4 and H5). MS (FAB, ^{192}Os): *m/z* 1072 (M^+), 1044 ($M^+ - CO$), 1016 ($M^+ - 2CO$), 988 ($M^+ - 3CO$), 960 ($M^+ - 4CO$), 932 ($M^+ - 5CO$), 904 ($M^+ - 6CO$), 876 ($M^+ - 7CO$), 848 ($M^+ - 8CO$), 820 ($M^+ - 9CO$).

Reaction of $Os_3(CO)_{10}(NCMe)(CNPr)$ with 1-Hydroxypyridine-2-thione. Under reaction conditions similar to those of $Os_3(CO)_{11}(CNCH_2Ph)$, complex $Os_3(CO)_{11}(CNPr)$ (150 mg, 0.158 mmol) afforded $Os_3(CO)_9(\mu\text{-H})(CNPr)(\eta^2\text{-}SC_5H_4N(O))$ (**4b**, 80 mg, 49%) and a pair of isomers $Os_3(CO)_9(\mu\text{-H})(CNPr)(\mu\text{-}\eta^1\text{-S-}C_5H_4N(O))$ (**6b**, 30 mg, 18%). Data for complex **4b**: ^1H NMR ($CDCl_3$) δ −13.44 (s, 1 H, μ-H), 0.99 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3), 1.73 (m, 2 H, CH_2CH_3), 3.86 (t, 2 H, $^3J_{HH}$ = 6.9 Hz, $CNCH_2$), 6.64 (t, 1 H, $^3J_{HH}$ = 7.3 Hz, H5), 7.12 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, H4), 7.72 (d, 1 H, $^3J_{HH}$ = 8.0 Hz, H3), 7.80 (d, 1 H, $^3J_{HH}$ = 6.6 Hz, H6); ^{13}C NMR ($CDCl_3$) δ 11.0 (CH_3), 22.1 (CH_2CH_3), 47.1 ($CNCH_2$), 159.0 (C2), 116.8 (C3), 130.0 (C4), 127.0 (C5), 138.0 (C6), 168.3, 170.4, 173.8, 174.8, 177.8, 181.8, 182.7, 184.3, and 185.2 (9 CO); IR (CH_2Cl_2) ν_{CN} = 2226 (m), ν_{CO} = 2091 (m), 2059 (s), 2025 (s), 2000 (s), and 1913 (m); MS (FAB, ^{192}Os) *m/z* 1024 (M^+). Anal. Calcd for $Os_3C_{18}H_{12}N_2O_{10}S$: C, 21.22; H, 1.19; N, 2.75. Found: C, 21.45; H, 1.06; N, 2.28. Data for complex **6b**: IR (CH_2Cl_2) ν_{CN} = 2203 (m), ν_{CO} = 2083 (m), 2058 (s), 2033 (s), 1997 (br), and 1966 (sh); MS (FAB, ^{192}Os) *m/z* 1024 (M^+), 996 ($M^+ - CO$), 968 ($M^+ - 2CO$), 940 ($M^+ - 3CO$); ^1H NMR ($CDCl_3$) δ −17.19 (s, 1 H, μ-H), 1.03 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3), 1.74 (m, 2 H, CH_2CH_3), 3.85 (t, 2 H, $^3J_{HH}$ = 6.9 Hz, $CNCH_2$), 7.05−7.20 (m, 2 H, H4 and H5), 7.40 (m, 1 H, $^3J_{HH}$ = 9.5 Hz, H3), 8.12 (m, 1 H, $^3J_{HH}$ = 6.3 Hz, H6); the other isomer (two isomers in a ratio of 1:1), δ −16.82 (s, 1 H, μ-H), 1.08 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.84 (m, 2H, CH_2CH_3), 3.94 (t, 2 H, $^3J_{HH}$ = 6.3 Hz, $CNCH_2$), 7.05−7.20 (m, 2 H, H4 and H5), 7.29 (d, 1 H, $^3J_{HH}$ = 9.5 Hz, H3), 8.10 (d, 1 H, $^3J_{HH}$ = 5.9 Hz, H6).

Thermolysis of Complex 1. A solution of **1** (226 mg, 0.231 mmol) in dry toluene (160 mL) was stirred at 80 °C for 3 h under nitrogen. The gases above the reaction were analyzed by GC/MS (SGE, 25QC3/BP-5, oven temperature 240 °C) which showed the formation of CO_2. The solvent was then removed under vacuum and the residue was chromatographed on a silica gel TLC plate (2-mm thickness). Elution with a mixture of CH_2Cl_2 and hexanes (1:4) gave compound $Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-pyS})$ (**7**, 19 mg, 0.020 mmol) in 9% yield,[10] whereas compound $Os_3(CO)_9(\mu\text{-OH})(\mu_3\text{-pyS})$ (**8**, 30 mg, 0.032 mmol) was obtained in 14% yield from an orange red band by elution with CH_2Cl_2. Data for **7**: IR (cyclohexane) ν_{CO} = 2086 (w), 2056 (vs), 2030 (vs), 2002 (vs), 1990 (s), 1966 (w), and 1953 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.02 (d, 1 H, ^3J = 5.6 Hz, H6), 7.53 (t, 1 H, ^3J = 7.6 Hz, H4), 7.38 (d, 1 H, ^3J = 7.8 Hz, H3), 7.05 (t, 1 H, ^3J = 6.5 Hz, H5), −15.15 (s, μ-H); MS (FAB, ^{192}Os) *m/z* 939 (M^+), 911 ($M^+ - CO$), 883 ($M^+ - 2CO$), 855 ($M^+ - 3CO$), 827 ($M^+ - 4CO$), 799 ($M^+ - 5CO$). Data for **8**: IR (CH_2Cl_2) 3599 (w), 3053 (w), 2080 (w), 2054 (vs), 2019 (s), 1976 (brs), 1942 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.90 (d, 1 H, ^3J = 5.3 Hz, H6), 7.48 (t, 1 H, ^3J = 7.6 Hz, H4), 7.27 (d, 1 H, ^3J = 8.0 Hz, H3), 6.99 (t, 1 H, ^3J = 6.5 Hz, H5), −1.49 (br, s, 1 H, hydroxyl proton). Results from a ^1H NMR experiment showed that the hydride resonance varied with temperature. ^{13}C NMR ($CDCl_3$): δ 191.14 (2 CO), 184.84 (2 CO), 183.34 (2 CO), 180.63 (CO or C2), 174.10 (2 CO), 183.59 (C2 or CO), δ 157.82, 135.23, 127.73, and 124.07 (aromatic). MS (FAB, ^{192}Os): *m/z* 955 (M^+), 927 ($M^+ - CO$), 899 ($M^+ - 2CO$), 871 ($M^+ - 3CO$). Anal. Calcd for $Os_3C_{14}H_5NO_{10}S$: C, 17.70; H, 0.53; N, 1.47. Found: C, 17.80; H, 0.54; N, 1.38.

Decarbonylation of Complex 1 and 2. To a solution of complex **1** (49 mg, 0.050 mmol) in CH_2Cl_2 (50 mL) was added a solution of Me_3NO (8.0 mg, 0.106 mmol) in CH_2Cl_2 (5.0 mL) at room temperature. The mixture was stirred for 2 h and purified through a silica gel column by the use of CH_2Cl_2 as eluent to afford complex **3** (36 mg) in 76% yield. Following the similar reaction conditions, the reaction of complex **2** (30 mg, 0.031 mmol) with Me_3NO (5.0 mg, 0.067 mmol) in CH_2Cl_2 (50 mL) gave complex **3** (15 mg) in 51% yield.

Crystallographic Structure Determination. Crystals suitable for X-ray diffraction studies of **1** were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the compound at −5 °C, crystals of **4b** and **5a** were grown from a mixture of CH_2Cl_2/*n*-hexane at −5 °C, and crystals of **8** were grown from a $CDCl_3$ solution of the compound in an NMR tube at 5 °C. Specimens of suitable quality were mounted in thin-walled glass capillaries and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) with $\theta/2\theta$ scan mode. Unit cells were determined and refined from 25 randomly selected reflections obtained by use of the CAD-4 automatic search, center, index, and least-squares routines. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Lorentz/polarization (*Lp*) and empirical absorption corrections on the bases of three azimuthal scans were applied to the data for each structure. Compounds **1** and **4b** were crystallized in the triclinic crystal system while complexes **5a** and **8** were crystallized in the monoclinic crystal system. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for **1** and **4b**. The systematic absences in the diffraction data of **5a** and **8** show the space group as $P2_1/n$ and $P2_1/c$, respectively. The structures were solved using the Patterson method. All remaining non-hydrogen atoms were located from the difference Fourier maps, and they were included in the final refinement cycles and refined by full-matrix least squares. The hydride peak in **1** was located and refined. All the data processing were carried out on a Microvax 3600 by use of the NRCC SDP program.[19]

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully acknowledged. We are also grateful to Professor A. J. Deeming for useful discussions.

Supporting Information Available: For **1**, **4b**, **5a**, and **8** tables of crystal and intensity collection data, atomic coordinates and *B* values, anisotropic thermal parameters, and bond lengths and angles (37 pages). Ordering information is given on any current masthead page.

OM9601763

(19) Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Clarendon: Oxford, England, 1985; pp 167−174.