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Reactions of Tp–Os nitrido complexes with the nucleophiles hydroxide and thiosulfate

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Dedicated to Professor Brian R. James on the occasion of his 70th birthday and in recognition of his many contributions to inorganic chemistry.

Abstract

The reaction between $TpOs(N)Cl_2$ (**1**) [Tp = hydrotris(1-pyrazolyl)borate] and aqueous ($^nBu_4N$)(OH) in THF-d_8 forms the nitrosyl complex $TpOs(NO)Cl_2$ (**5**) among other products, suggesting an initial hydroxide attack at the nitrido ligand. In contrast, the reaction of the acetate complex $TpOs(N)(OAc)_2$ (**2**) with NaOH in Me_2CO/H_2O yields the osmium bis-hydroxide complex $TpOs(N)(OH)_2$ (**3**), which has been structurally characterized by single-crystal X-ray diffraction. Acetate for hydroxide exchange could occur by ligand substitution or by nucleophilic attack at the carbonyl carbon of the acetate ligands (saponification). Reacting **2** with $Na^{18}OH$ in $H_2{}^{18}O/CD_3CN$ yields predominantly doubly ^{18}O-labeled $TpOs(N)(^{18}OH)_2$ (**3-$^{18}O_2$**) and unlabeled acetate, by ESI/MS and $^{13}C\{^1H\}$ NMR. This indicates that hydroxide reacts by substitution rather than by attack at the ligand. The reaction of **2** with the softer nucleophile thiosulfate occurs at the nitrido ligand, giving the thionitrosyl complex $TpOs(NS)(OAc)_2$ (**4**). Reacting **4** with NaOH in $(CD_3)_2CO/D_2O$ also generates the bis-hydroxide complex **3**.

Keywords: Osmium; Tp; Hydroxide; Nitrido; Acetate; Thionitrosyl; Nitrosyl

1. Introduction

Metal complexes typically involve electron-rich ligands binding to Lewis-acidic metal centers. Therefore, the addition of nucleophiles usually proceeds by attack at the metal center, while electrophiles typically add to ligands. In some complexes, however, these roles can be reversed. The nitrido ligand is interesting in this regard because it can react with both nucleophiles and electrophiles. Shapley and coworkers have reported that anionic Os^{VI}-nitrido complexes with electron-donating alkyl ligands react with electrophilic methylating agents $(Me_3O)(BF_4)$ or CF_3SO_3Me at the nitrido ligand to produce imido complexes $Os(NMe)R_4$ (R = Me, CH_2SiMe_3, CH_2CMe_3, or CH_2Ph) [1]. Recently, protonation of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ by HBF_4 or CF_3SO_3H has been found to occur at the nitrido ligand rather than at an alkyl group [2]. In contrast, the nitrido ligand in $TpOs(N)Cl_2$ (**1**) [Tp = hydrotris(1-pyrazolyl)borate] is electrophilic. For example, PPh_3 reacts rapidly with the nitride to form the phosphinidine complex $TpOs(NPPh_3)Cl_2$ [3], and PhMgCl and BPh_3 effect Ph^- addition to the nitrido, yielding $TpOs(NHPh)Cl_2$ after hydrolytic workup [4]. An unusual bicyclic Os-amido complex $TpOs(NC_6H_8)Cl_2$, is prepared from **1** and 1,3-cyclohexadiene [5]. In these latter cases, there is a two-electron reduction of the metal center, $Os^{VI} \rightarrow Os^{IV}$, as is common when a nucleophile adds to a ligand. A formal four-electron reduction to Os^{II} occurs when a chalcogen atom

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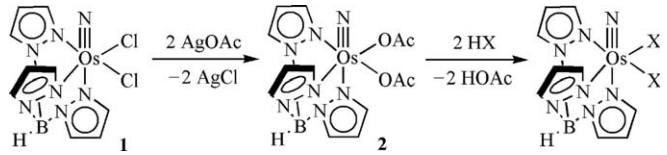


Scheme 1.

is transferred to the nitrido ligand in **1**, from Me_3NO or elemental sulfur or selenium, to give the chalconitrosyl complexes $TpOs(NE)Cl_2$ (E = O, S, or Se) [6].

Most of the reactions of **1** that we have examined occur at the nitrido ligand, while the chloride ligands remain inert. With the addition of AgOAc, however, the chloride ligands are replaced by acetate to form $TpOs(N)(OAc)_2$ (**2**) (Scheme 1) [7]. Under acidic conditions, the acetate ligands in **2** are labilized by protonation, allowing preparation of a series of $TpOs(N)X_2$ complexes using acidic HX reagents (X = Br, NO_3, O_2CCF_3, O_2CCCl_3, O_2CCBr_3, or X_2 = oxalate) [7]. Reported here are reactions of **2** and related compounds with the non-acidic nucleophilic reagents hydroxide and thiosulfate, leading to the syntheses of $TpOs(N)(OH)_2$ (**3**) and $TpOs(NS)(OAc)_2$ (**4**). The reactivity of **1**, **2**, and **3** with hydroxide, at the metal or at a ligand, is also described.

2. Results and discussion

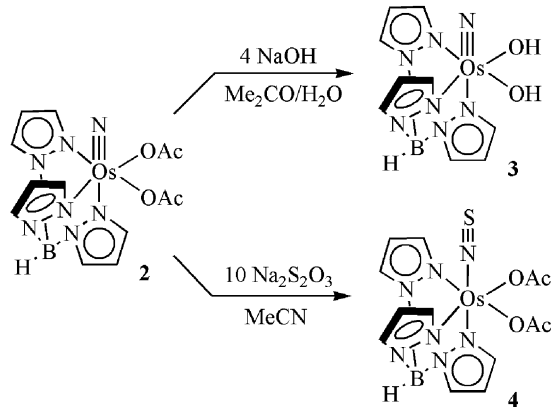
2.1. Synthesis and spectroscopic characterization of $TpOs(N)(OH)_2$ (3)

Stirring $TpOs(N)(OAc)_2$ (**2**) and 4 equiv. of NaOH in Me_2CO/H_2O at room temperature for 30 min yielded the orange bis-hydroxide complex $TpOs(N)(OH)_2$ (**3**) in 60% yield, isolated via silica gel chromatography (Scheme 2). The ^1H NMR spectrum of **3** displays a diamagnetic 2:2:2:1:1:1 integration pattern of six pyrazole resonances, and six pyrazole peaks are seen in the $^{13}C\{^1H\}$ NMR spectrum as well. Thus, **3** has C_s symmetry similar to **1**, **2**, and other $TpOs(N)X_2$ compounds [7]. A resonance at δ 5.09 observed for **3** in dry CD_2Cl_2 is assigned to the hydroxide protons. The addition of a drop of D_2O results in an upfield shift of this peak, which indicates rapid exchange between $TpOs(N)(OH)_2$ and water and confirms their assignment. The IR spectrum of **3** in KBr shows ν(O–H) at 3420 cm^{-1} and ν(Os≡N) at 1080 cm^{-1}, typical of $TpOs(N)X_2$ complexes [7]. The labeled compound $TpOs(^{15}N)(OH)_2$ (**3-^{15}N**) exhibits ν(Os≡^{15}N) at 1044 cm^{-1}, very close to the value of 1046 cm^{-1} calculated from a simple diatomic harmonic oscillator model [8]. The ESI/MS spectrum of **3** shows the most abundant peaks at 454 $[M+H]^+$, 476 $[M+Na]^+$, and 492 m/z $[M+K]^+$; **3-^{15}N** shows similar isotopic clusters one m/z unit greater. Electrochemical reduction of **3** in MeCN is irreversible at −1.53 V ($E_{p,c}$) versus $FeCp_2^{+/0}$, analogous to other $TpOs(N)X_2$ complexes [7].

High valent metal–hydroxide complexes are not so common because they often readily condense to μ-oxo derivatives. Other Os^{VI} examples include *trans*-$[OsO_2(OH)_4]^{2-}$ [9,10], *trans*-$[Os(N)(OH)(CN)_4]^{2-}$ [11], and *trans–cis*-$OsO_2(OH)_2$(phen), which can be converted to the bis-μ-oxo complex $[OsO_2(phen)(\mu\text{-}O)]_2$ in boiling water (phen = 1,10-phenanthroline) [12,13]. Related Os^{VI} and Ru^{VI} bis-μ-hydroxo dimeric complexes $[M(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$ (M = Ru or Os) [14], $[OsO_2L(\mu\text{-}OH)]_2^{2-}$, and $[Os(N)L(\mu\text{-}OH)]_2$ have also been described (H_2L = 1,2-bis(*p*-toluenesulfonylamido)benzene) [15]. The Os^{VIII} complexes $[OsO_4(OH)]^-$ and *cis*-$[OsO_4(OH)_2]^{2-}$ are hydroxide adducts of OsO_4 [9]. A Re^V analog of **3**, $Tp^{Me2}ReO(OH)_2$, has been prepared by reduction of $Tp^{Me2}ReO_3$ by PPh_3 in H_2O/THF [Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate][16].

2.2. X-ray structure of $TpOs(N)(OH)_2$ (3)

Crystals of **3** were grown from CH_2Cl_2/hexanes solutions, and the structure was solved by direct methods. There are two independent molecules in the unit cell, one of which is disordered about the quasi-threefold axis of the TpOs unit. The discussion that follows uses the metrical parameters (Table 1) of the non-disordered molecule, which is drawn in Fig. 1 (see Section 4.7 for selected crystallographic data). The ORTEP of **3** shows a distorted octahedral molecule with all of the ligands bent away from



Scheme 2.

Table 1
Selected bond lengths and angles for $TpOs(N)(OH)_2$ (**3**)[a]

Bond length (Å)		Bond angle (°)	
Os(1)–N(1)	2.084(10)	N(1)–Os(1)–N(3)	89.2(4)
Os(1)–N(3)	2.099(10)	N(3)–Os(1)–N(5)	78.5(4)
Os(1)–N(5)	2.328(9)	N(1)–Os(1)–N(7)	93.2(4)
Os(1)–N(7)	1.651(10)	N(3)–Os(1)–N(7)	90.7(4)
Os(1)–O(1)	1.941(8)	N(5)–Os(1)–N(7)	166.9(4)
Os(1)–O(2)	1.956(7)	O(1)–Os(1)–N(7)	106.0(4)
B(1)–N(2)	1.527(18)	O(2)–Os(1)–N(7)	102.6(4)
B(1)–N(4)	1.544(18)	O(1)–Os(1)–O(2)	87.7(3)
B(1)–N(6)	1.544(17)	O(1)–Os(1)–N(3)	163.3(4)
N(1)–N(2)	1.384(13)	O(2)–Os(1)–N(1)	164.1(3)
N(3)–N(4)	1.374(14)	O(2)–Os(1)–N(3)	88.3(4)
N(5)–N(6)	1.356(12)	O(2)–Os(1)–N(5)	84.6(3)

[a] Metrical data for the non-disordered molecule in the structure.

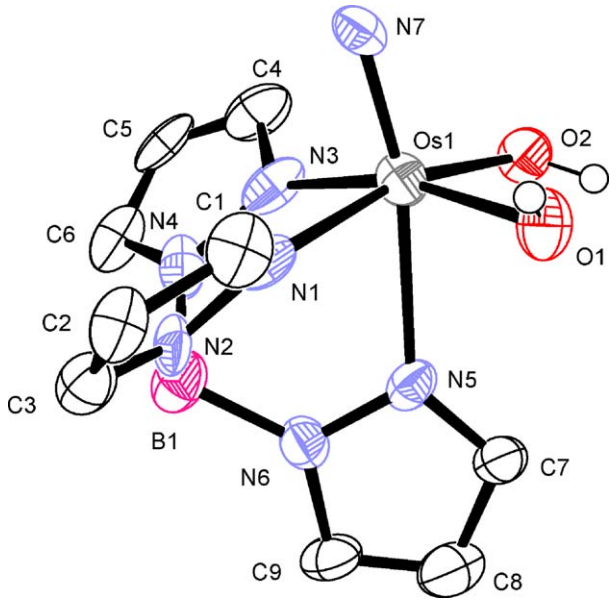


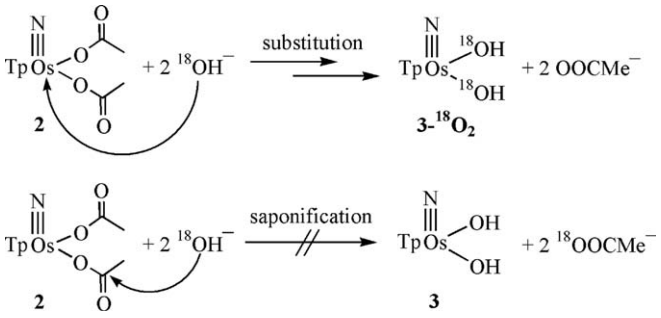
Fig. 1. ORTEP of the non-disordered molecule in the structure of $TpOs(N)(OH)_2$ (**3**). Hydrogen atoms are omitted for clarity, except for the hydroxides.

the nitrido N(7), typical of complexes with a single nitrido or oxo group [17]. The Os≡N distance of 1.651(10) Å is within the 1.602(20)–1.70(2) Å range of such bond lengths in $TpOs(N)X_2$ complexes ($X = O_2CCF_3$, NO_3, Cl, Me, Ph) [4a,7]. The Os–OH distances of **3** at 1.956(7) and 1.941(8) Å are shorter than those of *trans–cis*-$OsO_2(OH)_2$(phen) (1.982(4) and 1.984(5) Å) [12], *trans*-$[Os(N)(OH)(CN)_4]^{2-}$ (2.123(5) Å) [11], *trans*-$[OsO_2(OH)_4]^{2-}$ (2.03 Å) [9,10], and *cis*-$[OsO_4(OH)_2]^{2-}$ (2.10 and 2.17 Å) [9], and those of bridging hydroxide complexes [15].

2.3. ^{18}O-Labeled study: ligand substitution of $TpOs(N)(OAc)_2$ (2) and $Na^{18}OH$

The formation of **3** from **2** and NaOH is a formal substitution of hydroxide for acetate. This contrasts with reactions of other nucleophiles such as alkoxides, which do not substitute for acetate. We therefore considered two possible mechanisms for this reaction: saponification via an initial hydroxide attack at the carbonyl carbon of the acetate ligands, or direct substitution of hydroxide for acetate. The mechanisms can be distinguished by reacting **2** with $Na^{18}OH$. Ligand substitution would involve cleavage of the Os–O bonds to form $TpOs(N)(^{18}OH)_2$ (**3-$^{18}O_2$**) and unlabeled acetate, while saponification would retain the Os–O bonds and yield unlabeled **3** and singly ^{18}O-labeled $^{18}OOCMe^-$ (Scheme 3). A saponification mechanism has previously been indicated for hydroxide reactions with $[Co(NH_3)_5(O_2CCX_3)]^{2+}$ (X = H, Cl, or F) [18].

The reaction of **2** with $Na^{18}OH$ was conducted in CD_3CN instead of acetone, in order to eliminate the possible exchange of ^{18}O label with the solvent. Addition of 95%-enriched $Na^{18}OH$ to **2** in $H_2{}^{18}O/CD_3CN$ produced isotopically enriched **3**. The ESI/MS spectrum showed isotopic



Scheme 3.

patterns centered at 456/458 [**3-^{16}O^{18}O**+H/**3-$^{18}O_2$**+H]$^+$, 480 [**3-$^{18}O_2$**+Na]$^+$, and 496 *m/z* [**3-$^{18}O_2$**+K]$^+$ (Fig. 2a). The patterns for the Na^+ and K^+ clusters are roughly four *m/z* units greater than those of unlabeled **3** (Fig. 2b). Analysis of these clusters indicates an average isotopic composition of 84% **3-$^{18}O_2$**, 16% **3-^{18}O^{16}O**, and <3% **3-$^{16}O_2$** (each ±10%) (calculated isotopic patterns for **3-$^{18}O_2$** are shown in the insets of Fig. 2a). The protonated cluster at 456/458 *m/z* shows a higher abundance of the mono-labeled species [**3-^{18}O^{16}O**+H]$^+$ (456 *m/z*), because protonation occurs at a hydroxide ligand and facilitates ^{16}O exchange between [**3-$^{18}O_2$**+H]$^+$ and trace $H_2{}^{16}O$ in the electrospray solvent. In a control experiment, unlabeled **3** was reacted with $Na^{18}OH$ in $H_2{}^{18}O/CH_3CN$. The ESI/MS spectrum of the reaction solution showed predominately peaks for unlabeled **3**, with some ^{18}O exchange observed for the

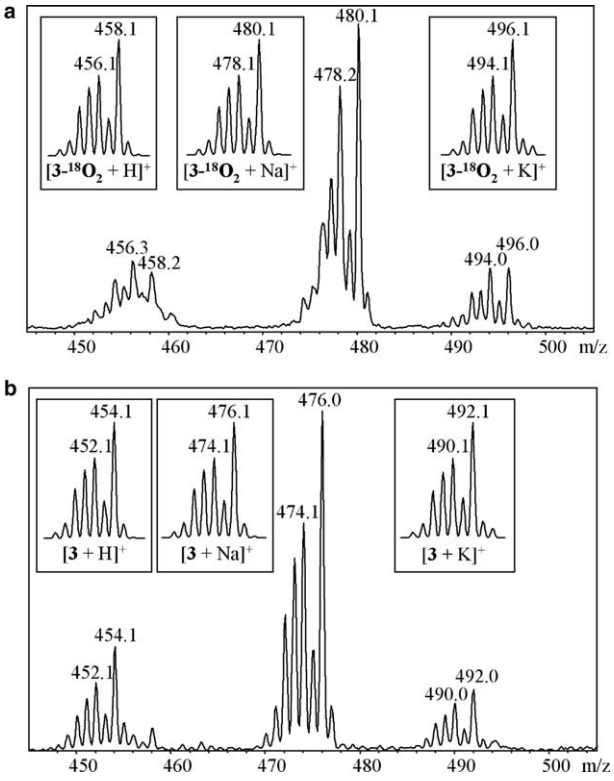


Fig. 2. Partial ESI/MS spectra of (a) labeled $TpOs(N)(^*OH)_2$ (mostly **3-$^{18}O_2$**) from $TpOs(N)(OAc)_2$ (**2**) + $Na^{18}OH$ and (b) $TpOs(N)(OH)_2$ (**3**) from **2** + NaOH, with calculated isotopic patterns shown in the insets.

protonated cluster $[\mathbf{3}+H]^+$ (454 m/z). This shows that **3** does not exchange with basic $H_2{}^{18}O/CH_3CN$ but that some exchange occurs under the acidic conditions of the electrospray experiment.

The isotopic enrichment of the acetate product was probed by $^{13}C\{^1H\}$ NMR, using the known upfield shift of the carboxylate carbons on substitution of ^{16}O for ^{18}O [19]. For aqueous acetic acid, this shift is reported to be 25 ppb at pH 2.0 and 27 ppb at pH 8.0 [20]. ^{18}O-Enriched sodium acetate was prepared from $H_2{}^{18}O$ hydrolysis of triethylorthoacetate ($MeC(OEt)_3$) [21], and the $^{13}C\{^1H\}$ NMR spectrum (Fig. 3a) showed two carboxylate ^{13}C resonances, for singly and doubly ^{18}O-labeled acetate (~40% $^{18}O_2$, ~50% $^{18}O^{16}O$, and <10% $^{16}O_2$, based on integration and Lorentzian line fitting [22]). The $^{13}C\{^1H\}$ NMR spectrum of the $\mathbf{2}+Na^{18}OH$ reaction mixture in $H_2{}^{18}O/CD_3CN$ showed a single peak in the carboxylate region (Fig. 3b). Spiking this solution with unlabeled NaOAc gave only a single carboxylate carbon resonance (Fig. 3c). Spiking with the $Na^{18}O_2CMe/Na^{18}O^{16}OCMe$ prepared from triethylorthoacetate showed three carboxylate ^{13}C peaks (Fig. 3d, $\Delta\delta \cong 27$ ppb), assigned to unlabeled, singly, and doubly ^{18}O-labeled acetate. Thus, we conclude that predominantly unlabeled acetate (<20% $^{18}O^{16}OCMe^-$, Fig. 3b) is formed in the reaction of **2** with $Na^{18}OH$. These experiments must be done by spiking with authentic samples because the absolute chemical shift of the carboxylate carbon varies from sample to sample (δ 180.2 ± 0.2), apparently due to changes in effective pH.

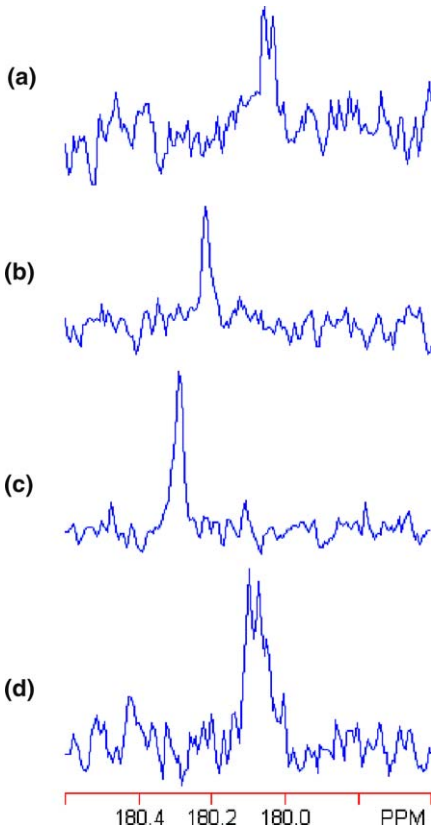


Fig. 3. Partial $^{13}C\{^1H\}$ NMR spectra of the carboxylate carbon resonances of free acetate prepared from (a) $H_2{}^{18}O + MeC(OEt)_3$, (b) TpOs(N)$(OAc)_2$ (**2**) + $Na^{18}OH$ in $H_2{}^{18}O/CD_3CN$, (c) **2** + $Na^{18}OH$ in $H_2{}^{18}O/CD_3CN$ then + $Na^{16}O_2CMe$, and (d) **2** + $Na^{18}OH$ in $H_2{}^{18}O/CD_3CN$ then + $Na^{18}O_2CMe/Na^{18}O^{16}OCMe$. All peaks appear at δ 180.2 ± 0.2, varying by a few tenths of ppm from sample to sample presumably depending on the pH.

In a control experiment, a reaction of **2** + $Na^{16}OH$ in $H_2{}^{16}O/CD_3CN$ was spiked with $Na^{18}O_2CMe/Na^{18}O^{16}OCMe$. The $^{13}C\{^1H\}$ NMR spectrum showed three carboxylate ^{13}C resonances, for all three isotopomers. Thus, under the reaction and spectroscopic conditions (ca. 12 h), exchange of the acetate oxygen atoms with the $H_2{}^{16}O$ solvent is too slow to significantly deplete the ^{18}O label from the acetate. If exchange with the excess water had been fast, only $^{16}O_2CMe^-$ would have been observed.

In sum, the ESI/MS and NMR data both indicate that $^{18}OH^-$ substitution for acetate occurs predominately with Os–O bond cleavage, yielding **3-$^{18}O_2$** and unlabeled acetate. The data rule out a saponification pathway, which would have yielded unlabeled **3** and $^{18}OOCMe^-$. The observation that hydroxide and not alkoxides substitute for acetate may be due to the small size of hydroxide.

2.4. Synthesis and spectroscopic characterization of TpOs(NS)$(OAc)_2$ (4)

Refluxing **2** and 10 equiv. of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in MeCN for 2 h yielded the blue Os^{II}-thionitrosyl complex TpOs(NS)$(OAc)_2$ (**4**) in 41% yield, isolated via silica gel chromatography (Scheme 2). As with **3**, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** indicate C_s symmetry. The EI/MS spectrum shows an isotopic cluster at 569 m/z (M^+ for **4**), which appears at 570 m/z for TpOs(^{15}NS)$(OAc)_2$ (**4-^{15}N**). The IR spectrum of **4** shows a band at 1278 cm^{-1}, which appears at 1257 cm^{-1} in **4-^{15}N**, consistent with a thionitrosyl ligand. This vibration likely has some of the character of a diatomic N–S stretch [ν(N≡S)] and some of the asymmetric stretch of a triatomic Os–N–S unit (see [23]). This is why a simple diatomic oscillator approximation overestimates the isotopic shift: calculated $\nu(^{15}N{\equiv}S) = 1248\ cm^{-1}$. The cyclic voltammogram of **4** in MeCN shows reversible oxidation and reduction waves centered at 0.96 and −1.32 V versus $FeCp_2{}^{+/0}$, respectively. These are ~0.2 V more negative than those of the chloride analog, TpOs(NS)Cl_2 ($E_{1/2}$ = 1.20, −1.15 V) [6], indicating stronger electron donation of acetate versus chloride ligands.

The thionitrosyl complex **4** is likely formed by direct sulfur atom transfer from thiosulfate to **2**. This is a formal four-electron reduction of the osmium, two-electron reduction of the central sulfur in thiosulfate, and a six-electron oxidation of the nitrido nitrogen atom. The use of thiosulfate as a sulfur atom donor to a nitrido ligand has previously been described in the formation of *mer*-$L_3Tc(NS)Cl_2$ (L = py, 4-Me-py, or 3,5-Me_2-py) from $(Bu_4N)[Tc(N)Cl_4]$, $Na_2S_2O_3$, and L [24]. We find that thiosulfate can also be used to convert **1** to TpOs(NS)Cl_2, which has previously been prepared

from **1** and propylene sulfide [6], S_8 [6], $CS_2 + N_3^-$ [25], or $Mo(N)(S_2CNEt_2)_3$ [26]. Closely related thionitrosyl Os complexes $[(tpm)Os(NS)Cl_2]^+$ (tpm = tris(1-pyrazolyl)methane) [25] and *trans*-$[(tpy)Os(NS)Cl_2]^+$ (tpy = 2,2′:6′,2″-terpyridine) [27] have also been reported. Dilworth et al. first synthesized thionitrosyl metal complexes $Mo(NS)(S_2CNR_2)_3$ (R = Me, Et, or $R_2 = (CH_2)_5$), from $Mo(N)(S_2CNR_2)_3$ and propylene sulfide or S_8 [28].

Crystals of **4** were grown from Me_2CO/Et_2O solutions, and the structure was examined by direct methods. The structure is disordered about a mirror plane containing C(1), C(2), Os(1), and C(13), with all of the other atoms being 50/50 disordered about this plane. The ORTEP diagram in Fig. 4 shows one set of atoms; a drawing showing all of the duplicated atoms is given in the Supporting information. Due to the extensive disorder, a large number of restraints were required to achieve a reasonable refinement. Thus, the bond lengths and angles are not well defined, and only evidence of connectivity is obtained (see Section 4.7 for selected crystallographic data).

2.5. Reactions of hydroxide with $TpOs(N)Cl_2$ (**1**), $TpOs(N)(OH)_2$ (**3**), and $TpOs(NS)(OAc)_2$ (**4**)

The reaction between **1** and 1.2 equiv. of aqueous (^{n}Bu$_4$N)(OH) in THF-d_8 immediately produces a number of products, including the known nitrosyl complex $TpOs(NO)Cl_2$ (**5**) in 24% yield by ^{1}H NMR integration. Complex **5** was identified by ^{1}H NMR and IR spectra (e.g., $\nu(N{\equiv}O) = 1832\ cm^{-1}$). It was previously prepared from **1** by oxygen transfer from Me_3NO [6], similar to the synthesis of $[(tpy)Os(NO)Cl_2]^+$ [29]. The reaction of **1** with NO also generates **5**, in a multi-step reaction [30]. Column chromatography separates a number of the species of this reaction. One of the paramagnetic products was

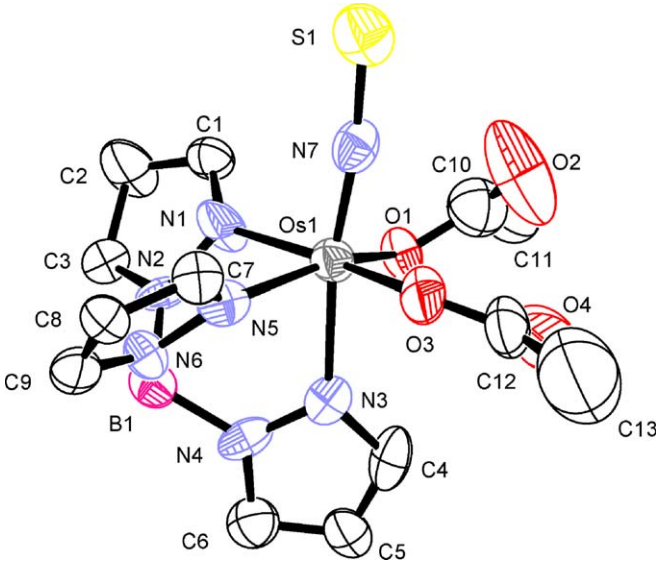
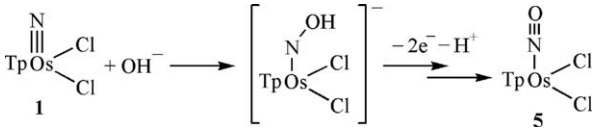


Fig. 4. ORTEP of one of the disordered positions of $TpOs(NS)(OAc)_2$ (**4**), with hydrogen atoms omitted for clarity.



Scheme 4.

identified by ESI/MS (976 *m*/*z*) and IR ($\nu(N{\equiv}N) = 2011\ cm^{-1}$) as the μ-$N_2$ Os^{II}–Os^{III} dimer $[TpCl_2Os–(\mu\text{-}N_2)–OsCl_2Tp]^-$, previously reported by Meyer et al. [31].

The reaction of hydroxide to **1** likely proceeds by an initial hydroxide attack at the nitrido ligand, parallel to the addition of other nucleophiles such as phosphines and carbanions [3,4]. This would give an anionic $Os^{IV}(NOH)^-$ intermediate, which must undergo subsequent loss of two electrons and a proton to form the nitrosyl product **5** (Scheme 4). The reducing equivalents are in part consumed in the formation of $[TpCl_2Os–(\mu\text{-}N_2)–OsCl_2Tp]^-$, which can also be formed by reduction of **1** with an one-electron reductant cobaltocene [31]. We were not able to determine the fate of the proton (there does not appear to be any gas evolution in the reaction). While no OsNOH complexes have been reported, $OsCl_2(NHOH)(NO)(PPh_3)_2$ is formed on protonation of $Os(NO)_2(PPh_3)_2$ with 2 equiv. of HCl [32].

Complex **3** does not react with 4 equiv. of NaOH in CD_3CN/D_2O over half an hour at room temperature. After 16 h, ^{1}H NMR indicated 19% decomposition of **3** and 11% of free Tp^-, which was confirmed by spiking with KTp. The addition of hydroxide to **3** is much slower than the analogous reaction of **1**. This is most likely because reduction of **3** is less favorable, as indicated by the irreversible electrochemical reduction potentials: $E_{p,c} = -1.53$ V for **3**, −1.34 V for **1** [7] (both versus $FeCp_2^{+/0}$ in MeCN). The more facile reduction of **1** favors hydroxide attack at the nitrido ligand to form the reduced $Os^{IV}(NOH)^-$ intermediate. Similarly, hydroxide does not rapidly react with the nitride in **2**, due to an even more negative $E_{p,c}$ (−1.83 V [7]). In contrast, hydroxide reacts rapidly with **2** at the osmium, likely because acetate is a better leaving group than the chloride ligands in **1**.

The thionitrosyl complex **4** also reacts with hydroxide. Reacting **4** with 4 equiv. of NaOH in $(CD_3)_2CO/D_2O$ gave a 26% yield of $TpOs(N)(OH)_2$ (**3**) in 30 min (by ^{1}H NMR). This conversion involves both desulfurization of the thionitrosyl to a nitrido ligand and substitution of the acetate ligands of **4**. The other osmium products were apparently paramagnetic, as **3** was the only Tp complex observed by ^{1}H NMR. ESI/MS confirmed **3** as a product, and showed a small amount of the nitrido-bis(acetate) complex **2** as well as other isotopic clusters for as yet unidentified osmium species. The fate of the sulfur is not evident. A possible pathway for this reaction would involve initial addition of hydroxide to the NS ligand in **4**, resulting in desulfurization and formation of **2**, which is then converted to **3**. Desulfurization of thionitrosyl metal complexes with phosphines as reductants has been accomplished in a number of

cases, including $Mo(NS)(S_2CNR_2)_3 + P^nBu_3 \rightarrow Mo(N)(S_2CNR_2)_3$ (R = Me, Et, or $R_2 = (CH_2)_5$) [28]. Treatment of $TpOs(NS)Cl_2$ with PPh_3 yields $TpOs(NPPh_3)Cl_2$ via the formation of $SPPh_3$ and **1**, which is rapidly trapped by a second equivalent of PPh_3 [6]. $[(tpm)Os(NS)Cl_2]^+$ reacts with PPh_3 analogously [25]. The reaction of $[(tpm)Os^{II}(NS)Cl_2]^+$ with Me_3NO gives $[(tpm)Os^{III}(NSO)Cl_2]$ by oxygen atom transfer to the sulfur [25]. Hydroxide is also known to add to the nitrogen of nitrosyl ligands in ruthenium complexes [33].

3. Conclusions

Hydroxide reacts with each of $TpOs(N)(OAc)_2$ (**2**) and $TpOs(NS)(OAc)_2$ (**4**) to form $TpOs(N)(OH)_2$ (**3**). An ^{18}O-labeling study indicates that the mechanism for the formation of **3** from **2** + hydroxide is direct substitution rather than saponification of the acetate ligands. In contrast, hydroxide does not substitute for the chloride ligands in $TpOs(N)Cl_2$ (**1**), but instead reacts rapidly with the nitride to form the nitrosyl complex $TpOs(NO)Cl_2$ (**5**) among other products. That hydroxide attacks the nitride ligand rapidly in **1** but not in **2** or **3** is likely due to the facility of reduction of the osmium centers in the three compounds, as indicated by the irreversible reduction potentials: $E_{p,c} = -1.34$ (**1**), -1.83 (**2**), and -1.53 V (**3**) (versus $FeCp_2^{+/0}$ in MeCN).

4. Experimental

All reactions were conducted under air, unless stated otherwise. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker spectrometers (300 and 500 MHz) at ambient temperatures and referenced to a residual solvent peak: δ (multiplicity, number of protons, assignment). All pyrazole resonances display $^3J_{HH} = 2$ Hz. Electrospray ionization mass spectra (ESI/MS) were obtained on a Bruker Esquire-LC ion trap mass spectrometer, and reported as *m*/*z* for the most isotopically abundant peak in an Os isotopic pattern. Samples were infused as a MeCN solution and acquired in positive or negative ionization mode. Electron impact mass spectra (EI/MS) were obtained on a Kratos Profile HV-3 direct probe instrument. UV–Vis spectra were acquired with a Hewlett–Packard 8453 diode array spectrophotometer in anhydrous CH_2Cl_2, and reported as λ_{max}/nm (ε/M^{-1} cm^{-1}). IR spectra were obtained as KBr pellets using Perkin–Elmer 1720 and Bruker Vector 33 FT-IR spectrometers, and are reported in cm^{-1} at 4 cm^{-1} resolution. Cyclic voltammetry (CV) measurements in 0.1 M ($^nBu_4N$)(PF_6)/MeCN were performed using a Pt disc working electrode, a Pt wire auxiliary electrode, and an Ag wire/$AgNO_3$ reference electrode with $FeCp_2$ as an internal standard, and potentials are reported versus $FeCp_2^{+/0}$. Elemental analyses were performed by Atlantic Microlab.

All reagent grade solvents were purchased from Fisher Scientific or EMD Chemicals. Deuterated solvents and $H_2{}^{18}O$ (95% ^{18}O-enrichment) were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 was dried over CaH_2 and vacuum transferred, and CD_3CN over CaH_2 then P_2O_5. ($^nBu_4N$)(OH) (40% wt. in H_2O), NaH, NaOH, and NaOAc (Aldrich) were used without purification. KTp [34], $TpOs(N)Cl_2$ (**1**) [4], $TpOs(N)(OAc)_2$ (**2**) [7], and $TpOs(^{15}N)(OAc)_2$ (**2-^{15}N**) [7] were prepared according to the literature procedures.

^{18}O-Enriched sodium acetate was prepared from $H_2{}^{18}O$ hydrolysis of triethylorthoacetate ($MeC(OEt)_3$) following the literature procedure [21]. ^1H NMR: 1.78 (s, CH_3). $^{13}C\{^1H\}$ NMR: 24.55 (CH_3); 180.042 ($C^{18}O_2$), 180.065 ($C^{18}O^{16}O$). Integration of the $^{13}C\{^1H\}$ NMR spectrum indicated an isotopic composition of ~40% $^{18}O_2$, ~50% $^{18}O^{16}O$, and <10% $^{16}O_2$. The NMR spectra were obtained in 350 μL CD_3CN + 100 μL $H_2{}^{16}O$ containing ~1 mg NaH, in order to be comparable to spectra obtained as part of the ^{18}O-labeling study described in Section 4.3.

4.1. Synthesis of $TpOs(N)(OH)_2$ (3)

A solution of **2** (240 mg, 0.45 mmol) and NaOH (71 mg, 1.78 mmol) in Me_2CO/H_2O (20 mL/2 mL) was stirred for 30 min. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with EtOAc/MeOH (90:10) and dried in vacuo at room temperature to yield 121 mg (0.27 mmol, 60%) of orange powder. ^1H NMR (CD_2Cl_2): 6.00 (t), 7.32 (d), 7.45 (d) (1H each, pz); 6.49 (t), 7.91 (d), 8.17 (d) (2H each, pz′); 5.09 (br s, 2H, OH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 105.69, 134.19, 141.51 (pz); 108.48, 138.54, 145.92 (pz′). ESI/MS: 454 $[M+H]^+$, 476 $[M+Na]^+$, 492 $[M+K]^+$. UV–Vis: 409 (210). IR: 1080 ν(Os≡N), 3420 ν(O–H). CV: $E_{p,c} = -1.53$ V ($Os^{VI/V}$). *Anal.* Calc. for $C_9H_{12}N_7O_2BOs$: C, 23.95; H, 2.68; N, 21.73. Found: C, 23.65; H, 2.57; N, 21.62%. $TpOs(^{15}N)(OH)_2$ (**3-^{15}N**) was synthesized analogously from **2-^{15}N**. ESI/MS: 455 $[M+H]^+$, 477 $[M+Na]^+$, 493 $[M+K]^+$. IR: 1044 ν(Os≡^{15}N).

4.2. Synthesis of $TpOs(NS)(OAc)_2$ (4)

A suspension of **2** (100 mg, 0.19 mmol) and $Na_2S_2O_3 \cdot 5H_2O$ (464 mg, 1.87 mmol) in MeCN (30 mL) was refluxed for 2 h. The mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2/MeOH (90:10). The blue fraction was stripped to dryness, re-precipitated with CH_2Cl_2/hexanes, filtered off, and dried in vacuo at 78 °C to yield 44 mg (0.08 mmol, 41%) of light blue powder. ^1H NMR (CD_2Cl_2): 6.27 (t), 7.65 (d), 7.78 (d) (1H each, pz); 6.42 (t), 7.77 (d), 8.01 (d) (2H each, pz′); 2.16 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 106.77, 136.50, 143.02 (pz); 108.30, 137.82, 145.79 (pz′); 23.55 (CH_3); 177.18 (CO_2). EI/MS: 569 $[M]^+$, 510 $[M-OAc]^+$, 464 $[M-OAc-NS]^+$. UV–Vis: 413 (260), 642 (190). IR: 1278 ν(N≡S). CV: $E_{1/2} = 0.96$ ($Os^{III/II}$), -1.32 V ($Os^{II/I}$). *Anal.* Calc. for $C_{13}H_{16}N_7O_4BSOs$: C, 27.52; H, 2.84; N, 17.28. Found:

C, 27.71; H, 2.81; N, 17.01%. TpOs(^{15}NS)(OAc)$_2$ (**4-^{15}N**) was synthesized analogously from **2-^{15}N**. EI/MS: 570 $[M]^+$, 511 $[M-OAc]^+$, 464 $[M-OAc-{}^{15}NS]^+$. IR: 1257 $\nu(^{15}N{\equiv}S)$.

4.3. ^{18}O-Labeled study: reaction of TpOs(N)(OAc)$_2$ (2) and Na^{18}OH

NaH (1 mg, 0.04 mmol) and dry CD_3CN (350 μL) were charged into a J-Young NMR tube, and $H_2{}^{18}O$ (100 μL) was added to generate a solution of $Na^{18}OH$ in $H_2{}^{18}O$/CD_3CN. Complex **2** (5.6 mg, 0.01 mmol) was then added, and the tube was shaken until a solution was formed, to generate TpOs(N)(*OH)$_2$ (mostly **3-^{18}O$_2$**) and $^{16}O_2CMe^-$. $^{13}C\{^1H\}$ NMR: 180.209 ($C^{16}O_2$). The tube was then spiked with $Na^{16}O_2CMe$ (3 mg), and $^{13}C\{^1H\}$ NMR was obtained: 180.281 ($C^{16}O_2$). The above experiment was duplicated except spiking with $Na^{18}O_2CMe/Na^{18}O^{16}OCMe$ (3 mg). $^{13}C\{^1H\}$ NMR: 180.044 ($C^{18}O_2$), 180.068 ($C^{18}O^{16}O$), 180.097 ($C^{16}O_2$). ESI/MS of **3-^{18}O$_2$**: 458 $[M+H]^+$, 480 $[M+Na]^+$, 496 $[M+K]^+$. In a control experiment, NaH (1 mg), CD_3CN (350 μL), $H_2{}^{16}O$ (100 μL), and **2** (5.6 mg) were added into a J-Young NMR tube to generate unlabeled **3** and $^{16}O_2CMe^-$, and the tube was spiked with $Na^{18}O_2CMe/Na^{18}O^{16}OCMe$ (3 mg). $^{13}C\{^1H\}$ NMR: 180.186 ($C^{18}O_2$), 180.214 ($C^{18}O^{16}O$), 180.234 ($C^{16}O_2$).

4.4. Reaction of TpOs(N)Cl$_2$ (1) with (^{n}Bu$_4$N)(OH)

In an NMR tube, (^{n}Bu$_4$N)(OH) (40% wt. in H_2O, 3.2 μL, 4.9 μmol) was added to a solution of **1** (2 mg, 4.1 μmol) in THF-d_8 (400 μL), containing a small amount of C_6H_6 as an internal standard. The tube was shaken, and a ^{1}H NMR spectrum showed TpOs(NO)Cl$_2$ (**5**) in 24% yield, based on integration relative to the standard. The product was confirmed by comparing its ^{1}H NMR spectrum with that of **5** prepared by the literature method [6]. ^{1}H NMR: 6.27 (t), 7.78 (d), 7.96 (d) (1H each, pz); 6.49 (t), 7.94 (d), 8.00 (d) (2H each, pz′). IR: 1832 $\nu(N{\equiv}O)$. Another product $[TpCl_2Os-(\mu\text{-}N_2)-OsCl_2Tp]^-$ [31] was identified by ESI/MS and IR; the observed ESI/MS isotopic pattern matched the calculated one. ESI/MS: 976 $[M]^-$. IR: 2011 $\nu(N{\equiv}N)$.

4.5. Reaction of TpOs(N)(OH)$_2$ (3) with NaOH

An NMR tube was charged with a solution of **3** (2 mg, 4.4 μmol) in CD_3CN/D_2O (350/100 μL) and a capillary containing $(Me_3Si)_2O$ in CD_3CN as a standard. After taking an ^{1}H NMR, 18 μL of 1 M NaOH/D_2O (18 μmol) was added. No change by NMR was detected after 30 min. 81% of **3** remained after 16 h, at which time 11% of free Tp^- was observed, based on integration relative to the standard. The identity of Tp^- was confirmed by spiking with authentic KTp. ^{1}H NMR of **3**: 6.02 (t), 7.29 (d), 7.55 (d) (1H each, pz); 6.52 (t), 8.03 (d), 8.19 (d) (2H each, pz′); free Tp^-: 6.13 (t), 7.31 (d), 7.46 (d) (1H each, pz).

4.6. Reaction of TpOs(NS)(OAc)$_2$ (4) with NaOH

An NMR tube was charged with a solution of **4** (2 mg, 3.5 μmol) in $(CD_3)_2CO/D_2O$ (350/100 μL) and a capillary containing $(Me_3Si)_2O$ in CD_3CN as a standard. After taking an ^{1}H NMR, 14 μL of 1 M NaOH/H_2O (14 μmol) was added, and the tube was allowed to stand for 30 min. ^{1}H NMR showed the formation of **3** in 26% yield, based on integration relative to the standard. The tube was spiked with authentic **3** to confirm the identity of the product. ^{1}H NMR: 5.97 (t), 7.33 (d), 7.55 (d) (1H each, pz); 6.53 (t), 8.07 (d), 8.23 (d) (2H each, pz′). ESI/MS: 454 $[M+H]^+$, 476 $[M+Na]^+$, 492 $[M+K]^+$.

4.7. X-ray structural determination of TpOs(N)(OH)$_2$ (3) and TpOs(NS)(OAc)$_2$ (4)

Crystals of **3** were obtained from slow evaporation of CH_2Cl_2/hexanes solutions and were mounted onto a glass capillary with oil. The data were collected on a Nonius Kappa CCD diffractometer. Selected crystallographic data for **3**: $C_9H_{12}BN_7O_2Os$, formula weight = 451.27, $0.14\times0.14\times0.10$ mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.3050(9)$ Å, $b = 14.6520(13)$ Å, $c = 15.0850(8)$ Å, $\beta = 115.984(4)°$, $V = 2643.5(4)$ Å^3, $\rho_{calc} = 2.268$ Mg m^{-3}, $Z = 8$, $2\theta_{max} = 4.14$–$24.71°$, Mo Kα radiation ($\lambda = 0.71070$ Å), $F(000) = 1696$, $T = 130(2)$ K, total/independent reflections = 21 816/4287 ($R_{int} = 6.18\%$), observed data = 7165 ($I > 2\ \sigma(I)$), restraints/parameters = 3/377, absorption correction: semi-empirical (*hkl*-SCALEPACK), maximum (minimum) transmission: 0.4450 (0.1037), R_1 (wR_2) = 5.21 (10.4)% for $I > 2\sigma(I)$, R_1 (wR_2) = 9.27 (11.5)% for all data, GOF = 0.958, largest difference in peak (hole) = 1.307 (−1.581) e Å^{-3}. Solution by direct methods (SIR-92) produced a complete heavy-atom phasing model consistent with the proposed structure. The heavy atoms were refined anisotropically by full-matrix least-squares, and the hydrogen atoms were placed using a riding model. However, one of the two chemically identical molecules was found to be disordered about the TpOs pseudo-threefold axis. O3b, O4b, and N14b of the minor form, 19.07(3)% of the molecules were refined isotropically with fixed thermal parameters (0.05).

Crystals of **4** were grown from slow evaporation of Me_2CO/Et_2O solutions. Selected crystallographic data for **4**: $C_{13}H_{16}BN_7O_4SOs$, formula weight = 567.44, $0.17\times0.17\times0.08$ mm, orthorhombic, space group *Pbcm* (No. 57), $a = 9.2380(6)$ Å, $b = 15.1010(10)$ Å, $c = 13.3830(10)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1867.0(2)$ Å^3, $\rho_{calc} = 2.019$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 2.20$–$28.31°$, Mo Kα radiation ($\lambda = 0.71073$ Å), $F(000) = 1088.0$, $T = 130(2)$ K, total/independent reflections = 29 644/2393 ($R_{int} = 7.44\%$), observed data = 4254 ($I > 2\sigma(I)$), restraints/parameters = 64/228, absorption correction: semi-empirical from equivalents, maximum (minimum) transmission: 0.58 (0.32), R_1 (wR_2) = 5.19 (11.9)% for $I > 2\ \sigma(I)$, R_1 (wR_2) = 12.7 (15.1)% for all data, GOF = 1.011, largest difference in

peak (hole) = 0.880 (−1.557) e Å^{-3}. The structure of **4** was solved by direct methods (SIR-97), and the heavy and hydrogen atoms were refined similar to those of **3**. The structure is disordered, and one set of the molecule is reflected into the other by application of a crystallographic mirror plane through C(1), C(2), Os(1), and C(13). Additional crystallographic information is given in the Supporting information.

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Appendix A. Supporting information

CCDC 243292 and 286567 contain the crystallographic data for **3** and **4**. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article, including additional discussion of the structure of **4**, with ORTEP and the unit cell diagrams showing all the disordered atoms can be found in the online version, at doi:10.1016/j.ica.2005.11.033.

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