Reactions of Triosmium Carbonyl Clusters with Thionylaniline. Crystal Structures of $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-(PhN)}_2SO)(\mu_3\text{-S})$, and $Os_3(CO)_8(NCMe)(\mu_3\text{-NPh})(\mu_3\text{-S})$

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Reaction of $Os_3(CO)_{12}$ with thionylaniline (PhN=S=O) in refluxing methylcyclohexane produces $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) in good yield. When $Os_3(CO)_{10}(NCMe)_2$ is treated with PhN=S=O at room temperature, compound **1** and $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-(PhN)}_2SO)(\mu_3\text{-S})$ (**2**) result. Compound **1** reacts with trimethylamine oxide in the presence of acetonitrile to give $Os_3(CO)_8(NCMe)(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**3**). Compounds **1**−**3** were characterized by mass, IR, and NMR spectroscopies, and their structures were determined by single-crystal X-ray diffraction. Crystal data for **1**: monoclinic ($C2/c$), $a = 16.603(7)$ Å, $b = 8.679(4)$ Å, $c = 29.009(6)$ Å, $\beta = 102.08(2)°$, $Z = 8$, R (R_w) = 0.036 (0.039). Crystal data for **2**: triclinic ($P\bar{1}$), $a = 9.723(4)$ Å, $b = 15.704(4)$ Å, $c = 18.455(7)$ Å, $\alpha = 113.17(3)°$, $\beta = 102.48(3)°$, $\gamma = 89.97(3)°$, $Z = 4$, R (R_w) = 0.030 (0.026). Crystal data for **3**: monoclinic ($P2_1/n$), $a = 18.792(3)$ Å, $b = 8.856(3)$ Å, $c = 26.210(9)$ Å, $\beta = 93.72(2)°$, $Z = 8$, R (R_w) = 0.066 (0.063).

Introduction

As part of our general interest in the systematic chemistry of homo- and heterocumulene ligands with metal clusters, the present research explores the reaction of thionylaniline with triosmium carbonyl clusters. Thionylaniline is a nonlinear heterocumulene, in which an oxygen atom of SO_2 is replaced by the imino group (=NR). There is evidence in the literature that the wealth of coordination chemistry displayed by SO_2 can be greatly extended by replacing the essentially "innocent" oxo species with more strongly donating groups such as imino and alkylidene (=CCR′).[1]

Thionylamine, RN=S=O, is readily synthesized in good yields by treating a secondary amine, RNH_2, with $SOCl_2$.[2] The three binding modes known for complexes of SO_2[3] have been observed in the interaction of thionylamine with low-valent mononuclear transition metal centers: σ,S-coplanar,[4] σ-S-pyramidal,[5] and π-N,S-bidentate.[4a,5a,b,6] However, the coordination chemistry of thionylamine with metal clusters has received little attention. We recently described reactions of triruthenium carbonyl clusters with thionylaniline, which led to the formation of several tri- and tetraruthenium cluster compounds containing sulfido, phenylimido, and thionylaniline ligands.[7] In the present research, we explored the reactions of thionylaniline with the analogous triosmium carbonyl clusters, where the stronger metal−metal bonds might reduce the tendency of the metal framework to rearrange upon reaction.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen with standard Schlenk and syringe techniques.[8] Solvents were distilled from the appropriate drying agent before use.[9] $Os_3(CO)_{12}$[10] and $Os_3(CO)_{10}(NCMe)_2$[11] were prepared by literature methods. ^{13}C-enriched $Os_3(CO)_{12}$ (ca. 10% ^{13}C) was prepared by heating a solution of $Os_3(CO)_{12}$ in decane at 140 °C for 48 h under 1.5 equiv of ^{13}CO in a Schlenk flask. Trimethylamine *N*-oxide dihydrate ($Me_3NO\cdot 2H_2O$) was purchased from Aldrich and sublimed (90 °C, 0.1 Torr) before use. Thionylaniline (PhN=S=O) and thin-layer chromatography (TLC) plates (2.5 mm silica gel on glass with 254 nm fluorescent indicator) from Aldrich were used as received.

Solution infrared data were recorded on a Bomem MB-100 FTIR spectrometer using a 0.1 mm path length CaF_2 cell. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 300 and 75.4 MHz, respectively. Electron impact (EI) and fast-atom-bombardment (FAB) mass spectra were obtained by Dr. D. L. Hung of the Northwestern University Analytical Services Laboratory on a VG 70/250 SE spectrometer. Elemental analyses were performed by Oneida Research Service, Whiteboro, NY.

Synthesis of $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$. A 300-mL Schlenk flask containing a sample of $Os_3(CO)_{12}$ (200 mg, 0.22 mmol) was purged with dry N_2. Methylcyclohexane (100 mL) and thionylaniline (52 μL, 0.45 mmol) were added, and the flask was attached to a reflux condenser equipped with a mineral oil bubbler. The mixture was heated to reflux (101 °C) under nitrogen for 16 h, cooled to room temperature under a slow N_2 purge, and then evaporated to dryness under vacuum. The residue was dissolved in dichloromethane and separated by TLC, with hexane/dichloromethane (3:1, v/v) as eluant. Isolation of the material

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from the major yellow band gave $Os_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (**1**) (150 mg, 0.16 mmol, 72%). IR (C_6H_{12}, ν_{CO}): 2098 (vw), 2076 (s), 2054 (vs), 2013 (vs), 2005 (s), 1997 (m), 1989 (m), 1979 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.03−6.60 (m, Ph). ^{13}C NMR ($CDCl_3$, 20 °C): δ 176.8 (2C), 175.5 (3C), 173.7 (2C), 170.5 (2C). Mass spectrum (EI): *m/z* 951 (M^+, ^{192}Os) and successive loss of 9 CO. Anal. Calcd for $Os_3C_{15}H_5O_9NS$: C, 19.05; H, 0.53; N, 1.48; S, 3.39. Found: C, 19.31; H, 0.29; N, 1.45; S, 2.93.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ and PhN=S=O. A 30-mL Schlenk flask containing a sample of $Os_3(CO)_{10}(NCMe)_2$ (100 mg, 0.107 mmol) was purged with N_2. Dichloromethane (20 mL) and thionylaniline (24 μL, 0.21 mmol) were added, and the mixture was stirred at room temperature for 30 min, at which point the IR spectrum showed no absorptions due to $Os_3(CO)_{10}(NCMe)_2$. The solution was concentrated to ca. 2 mL under reduced pressure and then subjected to TLC with hexane/dichloromethane (2:1, v/v) as eluant. Isolation of the material from the first yellow band afforded compound **1** (20 mg, 0.02 mmol, 20%). The second pale-yellow band yielded $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$ (**2**) (19 mg, 0.0175 mmol, 16%). IR (C_6H_{12}, ν_{CO}): 2107 (w), 2080 (s), 2049 (s), 2028 (m), 2022 (m), 2000 (s), 1990 (m), 1980 (sh), 1976 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.13−6.40 (m, Ph). Mass spectrum (EI): *m/z* 1090 (M^+, ^{192}Os) and successive loss of 9 CO. Anal. Calcd for $Os_3C_{21}H_{10}O_{10}N_2S_2$: C, 23.25; H, 0.93; N, 2.58. Found: C, 23.53; H, 0.71; N, 2.70. A crystal of **2**, suitable for X-ray diffraction, was grown from dichloromethane/hexane at −20 °C.

Synthesis of $Os_3(CO)_8(NCMe)(\mu_3\text{-}NPh)(\mu_3\text{-}S)$. A 100-mL Schlenk flask containing $Os_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (**1**) (120 mg, 0.127 mmol) was purged with N_2, and 10 mL of dichloromethane was added. A 30-mL Schlenk flask was charged with trimethylamine *N*-oxide (10 mg, 0.133 mmol) and acetonitrile (10 mL) under N_2, and the resulting solution was introduced over a period of 10 min into the flask containing compound **1**. The mixture was stirred under nitrogen at ambient temperature for another 40 min and then evaporated to dryness under vacuum. The residue was dissolved in dichloromethane and isolated by TLC, with dichloromethane/hexane (1:3, v/v) as eluant. The third, major yellow band afforded $Os_3(CO)_8(NCMe)(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (**3**) (63 mg, 0.066 mmol, 52%). IR (C_6H_{12}, ν_{CO}): 2080 (m), 2045 (vs), 2022 (vs), 2000 (vs), 1987 (w), 1980 (w), 1967 (s), 1953 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C): δ 6.99−6.74 (m, Ph), 1.92 (s, CH_3). Mass spectrum (FAB): *m/z* 964 (M^+, ^{192}Os), 923 (M^+ − MeCN), and successive loss of 8 CO. Anal. Calcd for $Os_3C_{16}H_8O_8N_2S$: C, 20.04; H, 0.84; N, 2.92. Found: C, 20.35; H, 0.81; N, 3.12.

X-ray Structure Determinations. Crystals suitable for X-ray diffraction were grown from a saturated hexane solution at −20 °C for compound **1** and dichloromethane/hexane at −20 °C for **2** and **3**. The unit cell constant determinations and data collection were performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Lattice parameters were determined from 25 randomly selected reflections with 2θ ranging from 20.2 to 23.2° (compound **1**), from 21.8 to 27.3° (compound **2**), and from 21.0 to 24.0° (compound **3**). The data were collected at −120 ± 1 °C using the $\omega-\theta$ scan technique to maximum 2θ values of 49.9, 52.0, and 49.1° for **1**−**3**, respectively. Scans of $(1.00 + 0.35 \tan\theta)°$ were made at a variable speed of 3.0−16.0°/min (in ω). The intensities of three representative reflections, which were measured after every 90 min of X-ray exposure time, remained constant throughout data collection, so no decay correction was applied. A summary of relevant crystallographic data for **1**−**3** is provided in Table 1. All calculations were carried out with the TEXSAN crystallographic software package of the Molecular Structure Corp. on a Micro VAX 3600 computer.

Structure Determination for $Os_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (1). An orange, transparent crystal of **1**, having approximate dimensions of 0.19 × 0.19 × 0.15 mm, was cut from a larger plate, mounted with grease on a glass fiber, and aligned on the diffractometer. On the basis of the systematic absences of *hkl* ($h + k \neq 2n$) and *h*0*l* ($l \neq 2n$), packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be *C*2/*c*. Of the 4004 reflections, 3873 were unique ($R_{int} = 0.080$). The linear absorption coefficient, μ, for Mo Kα radiation is 187.4 cm^{-1}. An empirical absorption correction using the program DIFABS[12] was applied, which resulted in transmission factors ranging from 0.50 to 1.00. The data were corrected for Lorentz and polarization effects. The data were also corrected for profile fitting. A correction for secondary extinction was applied. The structure was solved by direct methods[13] and expanded using Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2749 observed reflections ($I > 3.00\sigma(I)$) and 263 variable parameters.

Table 1. Crystallographic Data for Os3(CO)9(μ_3-NPh)(μ_3-S) (**1**), $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$ (**2**), and $Os_3(CO)_8(NCMe)(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (**3**)

	1	**2**	**3**
empirical formula	$Os_3C_{15}H_5O_9NS$	$Os_3C_{21}H_{10}O_{10}N_2S_2$	$Os_3C_{16}H_8O_8N_2S$
fw	945.87	1085.04	958.91
temp, °C	−120	−120	−120
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	16.603(7)	9.723(4)	18.792(3)
b, Å	8.679(4)	15.704(4)	8.856(3)
c, Å	29.009(6)	18.455(7)	26.210(9)
α, deg		113.17(3)	
β, deg	102.08(2)	102.48(3)	93.72(2)
γ, deg		89.97(3)	
V, Å^3	4087(2)	2518(1)	4352(1)
Z	8	4	8
$R(F)^a$	0.036	0.030	0.066
$R_w(F)^b$	0.039	0.026	0.063
GOF	2.05	1.31	2.48
D_{calc}, g·cm^{-3}	3.074	2.862	2.926
λ, Å	0.710 69	0.710 69	0.710 69

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o^2)$.

Structure Determination for $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$ (2). A yellow, translucent columnar crystal of **2** having approximate dimensions of 0.24 × 0.21 × 0.09 mm was cut from a larger sample, mounted on a glass fiber, and aligned on the diffractometer. On the basis of a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. Of the 10 198 reflections, 9872 were unique ($R_{int} = 0.044$). The linear absorption coefficient, μ, for Mo Kα radiation is 153.2 cm^{-1}, and an empirical absorption correction was applied to the data, resulting in transmission factors ranging from 0.90 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. Two independent molecules were refined in the asymmetric unit. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions but not refined. The final cycle of full-matrix least-squares refinement was based on 7182 observed reflections ($I > 3.00\sigma(I)$) and 686 variable parameters.

Structure Determination for $Os_3(CO)_8(NCMe)(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (3). A yellow, transparent, columnar crystal of **3** with approximate dimensions 0.33 × 0.11 × 0.07 mm was mounted on a glass fiber and aligned on the diffractometer. The systematic absences of *h*0*l* ($h + l \neq 2n$) and 0*k*0 ($k \neq 2n$) uniquely determined the space group to be $P2_1/n$. Of the 8018 reflections, 7937 were unique ($R_{int} = 0.108$). The linear absorption coefficient, μ, for Mo Kα radiation was 176.0 cm^{-1}. An analytical absorption correction was applied, which resulted in transmission factors ranging from 0.13 to 0.32. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The crystal moved during collection and had to be recentered. A different scale factor was applied to this second data set. The structure was solved by direct methods and expanded

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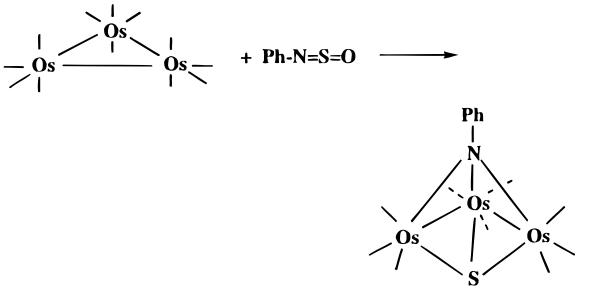
using Fourier techniques. Two independent molecules were refined in the asymmetric unit. Owing to the paucity of data, only osmium, sulfur, and oxygen atoms were refined anisotropically, while the rest of the non-hydrogen atoms were refined isotropically. Hydrogen atoms were included in idealized positions but not refined. The final cycle of full-matrix least-squares refinement was based on 4169 observed reflections ($I > 3.00\sigma(I)$) and 363 variable parameters.

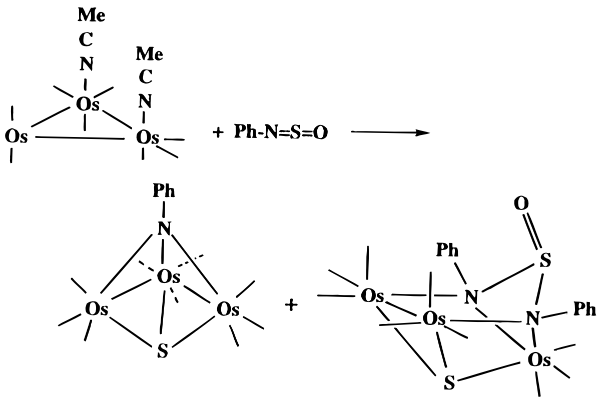
Results and Discussion

Syntheses of Compound 1 and Compound 2. Treatment of $Os_3(CO)_{12}$ with PhN=S=O in refluxing methylcyclohexane produces $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) in 72% yield (eq 1). A related complex $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$ was previously prepared from the thermal reaction of $Os_3(CO)_{12}$ and $Me_3SiN{=}S{=}NSiMe_3$.[15]



(1)

Reaction of the more labile acetonitrile-substituted complex $Os_3(CO)_{10}(NCMe)_2$ with PhN=S=O affords both compound **1** and $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-(PhN)}_2SO)(\mu_3\text{-S})$ (**2**) in moderate yields (eq 2). The ratio of **1** to **2** depends on the reaction temperature and is about 1:1 at 25 °C but increases to ca. 4:1 at 83 °C (refluxing 1,2-dichloroethane). We recently showed that treating $Ru_3(CO)_{10}(NCMe)_2$ with PhN=S=O at room temperature yields $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ as the only metal-containing product, and a reaction intermediate, $Ru_3(CO)_9(PhN{=}S)$ (via decarboxylation of $Ru_3(CO)_{10}(PhN{=}S{=}O)$), was proposed.[7] A similar conversion might occur in the present reaction to generate $Os_3(CO)_9(PhN{=}S)$, followed by N−S bond scission to yield **1**. When compound **1** is heated with a solution of PhNSO, no reaction is observed, so compound **2** is probably formed via coupling of $Os_3(CO)_9(PhN{=}S)$ with another PhNSO molecule, accompanied by N−S bond breaking (Scheme 1). A plausible alternative pathway for the formation of **2** is the successive replacement of the acetonitrile ligands by PhNSO to give $Os_3(CO)_{10}(PhN{=}S{=}O)_2$, followed by ligand coupling, decarboxylation, and N−S bond scission.



(2)

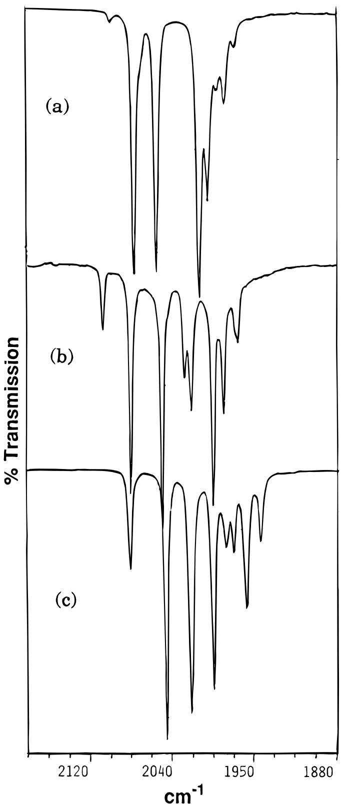
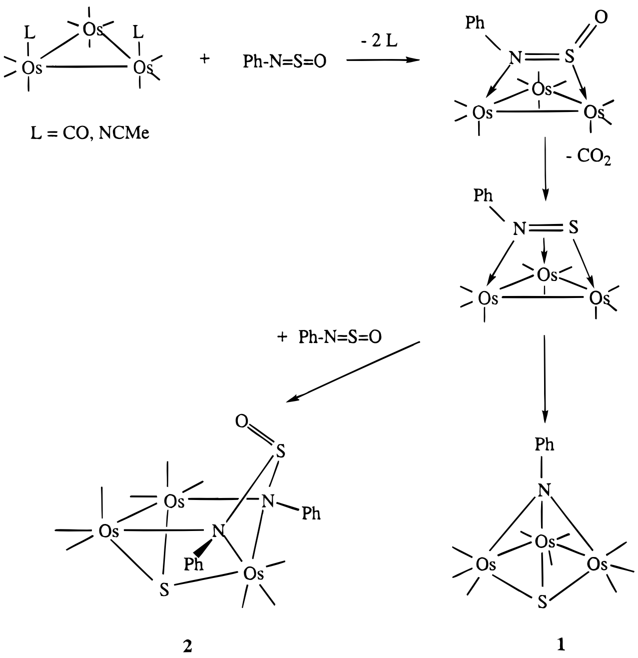


Figure 1. IR spectra in the carbonyl region of (a) $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**), (b) $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-(PhN)}_2SO)(\mu_3\text{-S})$ (**2**), and (c) $Os_3(CO)_8(NCMe)(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**3**).

Scheme 1



Characterization of 1. Compound **1** forms air-stable, orange crystals and has been characterized by mass, IR, and ^1H and ^{13}C NMR spectroscopy and by elemental analyses. The EI mass spectrum gives a molecular ion peak at m/z 951 for the $^{192}Os_3$ metal core with ion multiplets corresponding to loss of nine carbonyls. The isotopic distribution of the envelope surrounding the m/z 951 molecular ion matches that calculated for the formula of **1**. The IR absorptions in the carbonyl region of **1** (Figure 1a) show a pattern similar to that recorded for $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$,[7] whereas the triosmium analogue Os_3-

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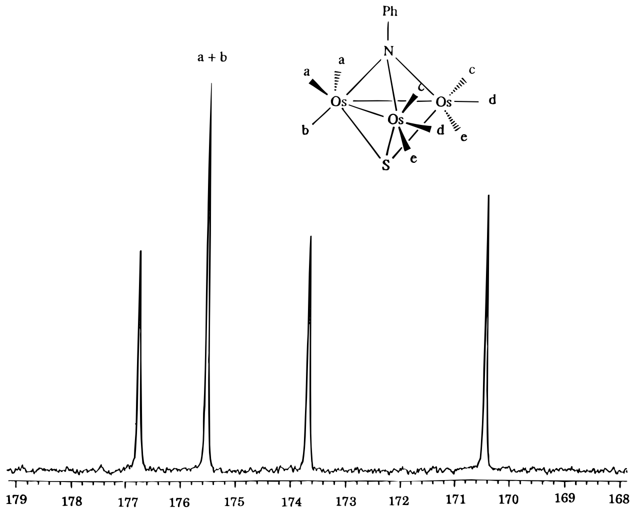

Figure 2. ^{13}C NMR spectrum of $Os_3(*CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1***) in $CDCl_3$ at 25 °C.

$(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$ was found to display a simpler pattern, with only five absorption peaks ranging from 2065 to 1978 cm^{-1}.[15]

The ^{13}C NMR spectrum of ^{13}C-enriched $Os_3(*CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1***, ca. 10% ^{13}CO) in $CDCl_3$ at 20 °C is shown in Figure 2. The carbonyl carbon resonances split into a 2:3:2:2 pattern in the range of δ 177−170, implying a time-averaged C_s symmetry for the molecule. Thus, the signal at δ 175.5 can be assigned to the three carbonyl carbons in the central $Os(CO)_3$ group, which presumably equilibrate via 3-fold rotation. The signals at δ 176.8, 173.7, and 170.5 are assigned to the remaining three pairs of carbonyls. It has been shown that the energy barrier for carbonyl 3-fold rotation decreases dramatically as the coordination number of the metal center changes from 6 to 7.[16] In **1**, the central and external osmium atoms are seven- and six-coordinate, respectively. The resonance pattern remains unchanged from −65 to +70 °C, with no indication of carbonyl exchange in the external $Os(CO)_3$ units or Os−Os bond reformation within the molecule. In contrast, the variable-temperature ^{13}C NMR study for the analogous complex $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$ consisted of a slow-exchange spectrum at −40 °C with the carbonyl carbon resonances in a 1:2:2:2:2 pattern, which equilibrated to give a single resonance at ca. 70 °C.[15] A reversible closing/opening process of the Os−Os bonds was proposed. It is obvious that differences in electron-donating ability and steric bulk between trimethylsilyl and phenyl groups affect the solution behavior of **1** and $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$, but the details are not clear.

Crystal Structure of 1. The X-ray structure of **1** confirms local C_s symmetry for the molecular skeleton, which was indicated by the ^{13}C NMR. The ORTEP drawing is shown in Figure 3, while the selected bond distances and bond angles are collected in Table 2. This complex consists of an open triangular cluster of three $Os(CO)_3$ units with triply-bridging phenylimido and sulfido groups on opposite sites of the Os_3 triangle. Compound **1** is structurally similar to $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$,[15] $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$,[7] $Fe_3(CO)_9(\mu_3\text{-NTol})(\mu_3\text{-S})$,[17] $M_3(CO)_9(\mu_3\text{-NPh})_2$ (M = Fe,[18] Ru[19]), and $M_3(CO)_9(\mu_3\text{-S})_2$ (M = Fe,[20] Ru,[21] Os[22]), which contain 50 cluster valence electrons and require only two metal−metal bonds to satisfy the 18-electron rule on each metal atom.

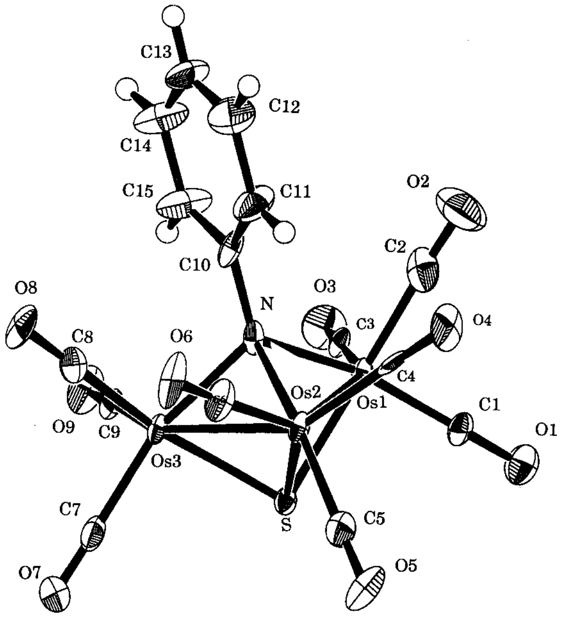

Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**)

	Distances		
Os1−Os2	2.754(1)	Os2−Os3	2.7538(8)
Os1−N	2.06(1)	Os2−N	2.14(1)
Os3−N	2.10(1)	Os1−S	2.372(4)
Os2−S	2.421(4)	Os3−S	2.373(4)
N−C10	1.46(2)	Os1−C1	1.88(2)
Os1−C2	1.91(2)	Os1−C3	1.85(2)
Os2−C4	1.94(2)	Os2−C5	1.92(2)
Os2−C6	1.92(2)	Os3−C7	1.92(2)
Os−C8	1.89(2)	Os3−C9	1.90(2)
	Angles		
Os1−Os2−Os3	78.26(2)	Os1−Os2−N	47.8(3)
Os2−Os1−N	50.2(3)	Os2−Os3−N	50.0(3)
Os3−Os2−N	48.8(3)	Os1−N−Os2	82.0(4)
Os1−N−Os3	113.5(6)	Os2−N−Os3	81.2(4)
Os1−N−C10	122.1(9)	Os2−N−C10	127.0(9)
Os3−N−C10	119.3(9)	Os1−Os2−S	54.10(9)
Os2−Os1−S	55.78(9)	Os2−Os3−S	55.77(9)
Os3−Os2−S	54.12(8)	Os1−S−Os2	70.1(1)
Os1−S−Os3	94.2(1)	Os2−S−Os3	70.1(1)
N−Os1−S	74.2(4)	N−Os2−S	71.9(3)
N−Os3−S	73.5(3)	Os2−Os1−C1	113.4(5)
Os2−Os1−C2	107.1(5)	Os2−Os1−C3	147.0(4)
S−Os1−C1	94.1(5)	S−Os1−C2	162.6(5)
S−Os1−C3	103.3(5)	N−Os1−C1	163.3(6)
N−Os1−C2	97.6(6)	N−Os1−C3	102.5(5)
Os1−Os2−C4	82.3(5)	Os1−Os2−C5	121.6(5)
Os1−Os2−C6	143.3(5)	Os3−Os2−C4	147.6(4)
Os3−Os2−C5	121.8(5)	Os3−Os2−C6	82.9(4)
S−Os2−C4	129.1(5)	S−Os2−C5	91.8(5)
S−Os2−C6	132.1(5)	N−Os2−C4	99.3(6)
N−Os2−C5	163.6(6)	N−Os2−C6	96.6(6)
Os2−Os3−C7	112.4(5)	Os2−Os3−C8	105.7(4)
Os2−Os3−C9	145.7(5)	S−Os3−C7	94.0(4)
S−Os3−C8	161.4(4)	S−Os3−C9	102.4(4)
N−Os3−C7	162.1(5)	N−Os3−C8	96.0(6)
N−Os3−C9	101.3(6)		

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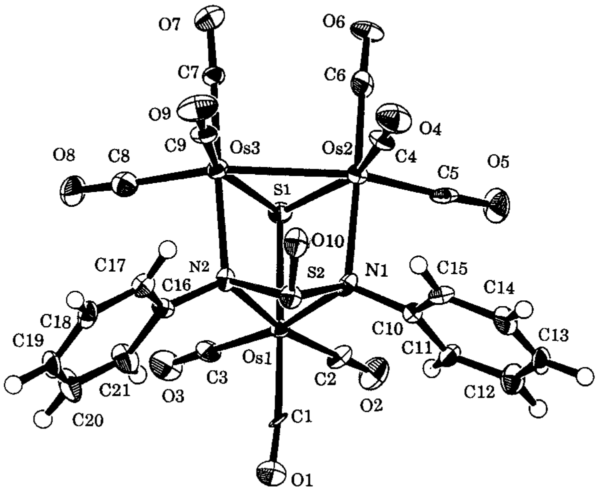

Figure 4. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

The two osmium−osmium lengths in **1** are about equal, being 2.754 ± 0.001 Å. Each osmium atom is associated with three terminal carbonyl ligands. The Os−CO distances to the central Os2 atom, averaging 1.93(2) Å, are slightly longer than those to the external Os3 and Os1 atoms, averaging 1.90(2) and 1.88(2) Å, respectively. The C−O distances range from 1.11(2) to 1.17(2) Å, averaging 1.14(2) Å, while the Os−C−O angles are in the range 177(1)−179(1)°. The phenylimido and sulfido groups cap opposite Os_3 faces asymmetrically. The lengths for Os2 bonds to N and S (2.14(1) and 2.421(4) Å, respectively), are longer than those to the Os3 atom (2.10(1) and 2.373(4) Å) and the Os1 atom (2.06(1) and 2.372(4) Å). This difference is attributed to the formal seven-coordination around Os2 as compared with six-coordination for the other two osmium atoms.

Characterization of 2. Compound **2** forms air-stable, yellow crystals. The IR spectrum (Figure 1b) shows a pattern of nine carbonyl stretching peaks, compared with eight noted above for **1**. The ^1H NMR spectrum of **2** includes a complex multiplet ranging from δ 7.13 to 6.40 for the phenyl proton resonances. The EI mass spectrum shows the parent ion at m/z 1090 (^{192}Os), corresponding to the mass of **1** plus a PhNSO molecule, and ions corresponding to the loss of nine carbonyls. The C, H, and N elemental analyses are consistent with the stoichiometry $Os_3(CO)_9(PhNS)_2O$. Due to the absence of diagnostic spectral features to reveal the structure of **2**, a single-crystal X-ray diffraction study was performed.

Crystal Structure of 2. There are two crystallographically independent molecules in the asymmetric unit, which are structurally equivalent, and the ORTEP diagram of one of these is illustrated in Figure 4. Selected bond lengths and angles are collected in Table 3.

Compound **2** consists of a cluster of three $Os(CO)_3$ groups which are linked together by one Os−Os bond, a triply-bridging sulfido (S), and a triply-bridging bis(phenylimino)oxo-λ^6-sulfane ($(PhN)_2S{=}O$) group. The coordination about each osmium atom can be described as a distorted octahedron. If the μ_3-S and μ_3-η^2-$(PhN)_2SO$ ligands are counted as four- and six-electron donors, respectively, the cluster valence electron count is 52. This electron count requires only one metal−metal bond to provide an 18-electron configuration on each osmium atom, in agreement with the structural observations.

The osmium−osmium bond distance found for **2** (Os2−Os3 = 2.7787(7) Å) is significantly shorter than values found in the parent compound $Os_3(CO)_{12}$[23] (Os−Os(av) = 2.877(3) Å). Each osmium atom is associated with three terminal carbonyls in a *facial* configuration. The average Os−CO distance is 1.91 ± 0.01 Å and average C−O distance is 1.14 ± 0.01 Å, while all Os−C−O angles are close to linear (172.6(8)−179(1)°).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$ (**2**)

Distances			
Os2−Os3	2.7787(7)	Os1−N1	2.192(7)
Os1−N2	2.186(7)	Os2−N1	2.254(8)
Os3−N2	2.233(8)	Os1−S1	2.421(3)
Os2−S1	2.395(2)	Os3−S1	2.400(3)
N1−S2	1.712(8)	N2−S2	1.758(7)
S2−O10	1.455(6)	N1−C10	1.46(1)
N2−C16	1.47(1)	Os1−C1	1.95(1)
Os1−C2	1.91(1)	Os1−C3	1.924(9)
Os2−C4	1.89(1)	Os2−C5	1.94(1)
Os2−C6	1.90(1)	Os3−C7	1.88(1)
Os3−C8	1.94(1)	Os3−C9	1.90(1)

Angles			
S1−Os1−N1	83.0(2)	S1−Os1−N2	82.4(2)
S1−Os1−C1	176.5(3)	S1−Os1−C2	90.1(3)
S1−Os1−C3	89.6(3)	N1−Os1−N2	67.3(2)
N1−Os1−C1	95.2(3)	N1−Os1−C2	103.8(3)
N1−Os1−C3	167.7(3)	N2−Os1−C1	94.2(3)
N2−Os1−C2	168.9(3)	N2−Os1−C3	102.1(3)
C1−Os1−C2	93.2(4)	C1−Os1−C3	91.7(4)
C2−Os1−C3	85.9(4)	Os3−Os2−S1	54.67(6)
Os3−Os2−N1	85.3(2)	Os3−Os2−C4	100.5(3)
Os3−Os2−C5	158.3(3)	Os3−Os2−C6	93.0(3)
S1−Os2−N1	82.3(2)	S1−Os2−C4	155.1(3)
S1−Os2−C5	103.7(3)	S1−Os2−C6	92.9(3)
N1−Os2−C4	94.4(4)	N1−Os2−C5	90.4(3)
N1−Os2−C6	175.0(3)	C4−Os2−C5	101.0(4)
C4−Os2−C6	90.5(4)	C5−Os2−C6	89.5(4)
Os2−Os3−S1	54.50(6)	Os2−Os3−N2	85.6(2)
Os2−Os3−C7	92.6(3)	Os2−Os3−C8	153.8(3)
Os2−Os3−C9	102.3(3)	S1−Os3−N2	81.9(2)
S1−Os3−C7	97.0(3)	S1−Os3−C8	99.3(3)
S1−Os3−C9	156.6(3)	N2−Os3−C7	178.2(3)
N2−Os3−C8	90.5(4)	N2−Os3−C9	94.9(4)
C7−Os3−C8	91.0(4)	C7−Os3−C9	85.6(4)
C8−Os3−C9	103.9(4)	Os1−N1−Os2	102.5(3)
Os1−N1−S2	93.1(3)	Os1−N1−C10	125.6(6)
Os2−N1−S2	115.1(4)	Os2−N1−C10	110.8(6)
S2−N1−C10	109.0(6)	Os1−N2−Os3	103.6(3)
Os1−N2−S2	92.1(3)	Os1−N2−C16	124.0(6)
Os3−N2−S2	114.5(4)	Os3−N2−C16	115.5(5)
S2−N2−C16	105.2(6)	Os1−S1−Os2	92.15(9)
Os1−S1−Os3	92.16(9)	Os2−S1−Os3	70.84(7)
O10−S2−N1	110.9(4)	O10−S2−N2	110.9(4)
N1−S2−N2	88.7(4)		

The geometry of **2** can be viewed as an opened envelope consisting of an Os_3N_2 unit, bridged by μ-SO and μ_3-S fragments. The Os2, Os3, N2, and N1 atoms are essentially coplanar, as evidenced by their torsional angles (0.7 ± 0.3°), and the Os1 atom is tilted 42.7(3)° away from this plane. The dihedral angle between the N1−S2−N2 plane and the Os2−Os3−N2−N1 plane is 56.5(7)°. The distances from N1 and N2 to Os2 and Os3 (2.254(8) and 2.233(8) Å) are slightly longer than the distances from N1 and N2 to Os1 (2.192(7) and 2.186(7) Å). The N1−S2−O10 and N2−S2−O10 angles are equal, 110.9(4)°, and the N1−S2−N2 angle is 88.7(4)°, indicating a distorted pyramidal conformation about the S2 atom. The S2−O10 distance of 1.455(6) Å is characteristic of a sulfur−oxygen double bond. The sulfido ligand bridges the three osmium atoms unequally, where the bond lengths in decreasing order are S1−Os1 = 2.421(3)Å, S1−Os3 = 2.400(3) Å, and S1−Os2 = 2.395(2) Å.

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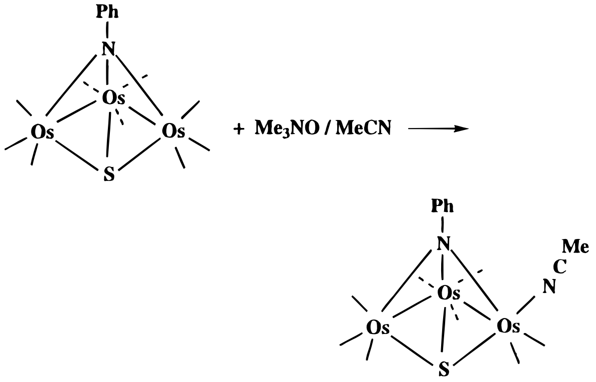
Synthesis and Characterization of 3. Reaction of $Os_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) and 1 equiv of Me_3NO in acetonitrile/dichloromethane solution affords $Os_3(CO)_8(NCMe)(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**3**) in 52% yield (eq 3). Apparently, electrophilic attack of Me_3NO occurs at a carbonyl ligand to liberate CO_2 and Me_3N, and the empty coordination site is then occupied by a MeCN ligand. There was no indication of electrophilic attack of the amine oxide on the sulfido atom to generate a sulfoxide species.



(3)

Compound **3** forms an air-stable, yellow crystalline solid, which can be purified by TLC and recrystallization from a hexane/dichloromethane solution at −20 °C. The FAB mass spectrum shows the molecular ion peak at m/z = 964, for ^{192}Os, and ions corresponding to loss of an acetonitrile and eight carbonyls. However, the EI mass spectrum displays the highest mass at m/z 923, corresponding to the $M^+ - MeCN$ fragment. The ^{1}H NMR spectrum includes a multiplet in the range δ 6.99−6.74, assigned to the phenyl protons, and a singlet at δ 1.92, assigned to the acetonitrile protons. The IR spectrum in the carbonyl region (Figure 1c) shows eight absorption peaks ranging from 2080 to 1953 cm^{-1}. These carbonyl absorptions are shifted to lower energy than those of **1** (Figure 1a), consistent with the stronger σ-donor and weaker π-acceptor ability of the NCMe ligand compared with CO.[24]

Crystal Structure of 3. There are two independent molecules in the asymmetric unit, which are essentially enantiomers of each other. The ORTEP drawing of one of these is shown in Figure 5. Table 4 contains the selected bond lengths and bond angles. The overall geometry of the complex is similar to that of the parent compound **1**, except that an acetonitrile ligand replaces one of the axially-positioned carbonyl ligand (*cis* to the Os−Os vector) on the external $Os(CO)_3$ units. The Os−Os edge adjacent to the acetonitrile ligand (Os−Os2 = 2.806(2) Å) is considerably longer than the other edge (Os2−Os3 = 2.721(2) Å), in agreement with the stronger net donor strength of the NCMe ligand relative to CO.

The Os2 and Os3 atoms are each linked to three terminal carbonyl ligands, and Os1 has only two. The Os−CO lengths associated with Os1 and Os3 atoms are slightly different, ranging from 1.81(4) to 1.91(5) Å, while those associated with the Os2 atom are more diverse, ranging from 1.74(5) Å to 1.99(5) Å. The C−O distances range from 1.27(5) Å (C3−O3) to 1.09(4) Å (C8−O8), averaging 1.16(4) Å, and the Os−C−O angles are in the range 170(3)−177(3)°. The phenylimido and sulfido groups triply-bridge the opposite Os_3 faces asymmetrically, so that the N2−Os and S1−Os interactions with the central Os2 atom are stronger than those with the external Os1 and Os3 atoms. The mean N−Os distance to the imido group (2.14 ± 0.03 Å) is longer than the Os−N distance to the acetonitrile ligand (2.03 ± 0.02 Å).

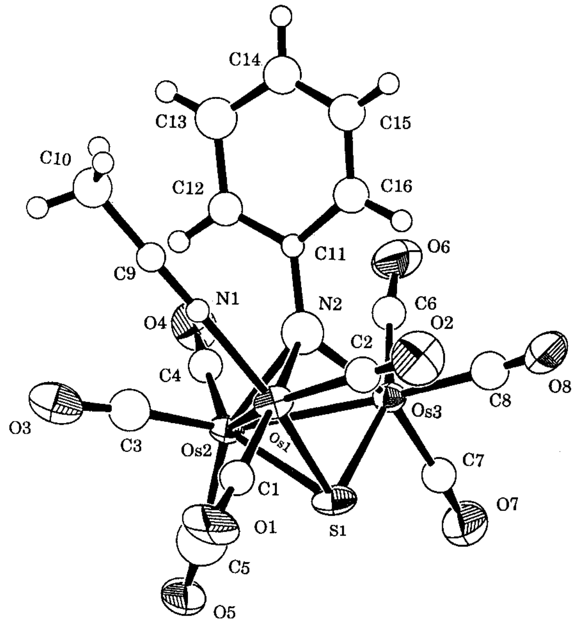


Figure 5. ORTEP diagram of $Os_3(CO)_8(NCMe)(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_3(CO)_8(NCMe)$ $(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**3**)

Distances			
Os1−Os2	2.806(2)	Os2−Os3	2.721(2)
Os1−N1	2.03(2)	Os1−N2	2.11(3)
Os1−S1	2.32(1)	Os1−C1	1.90(4)
Os1−C2	1.89(4)	Os2−N2	2.20(3)
O2−S1	2.44(1)	Os2−C3	1.74(5)
Os2−C4	1.83(4)	Os2−C5	1.99(5)
Os3−N2	2.11(3)	Os3−S1	2.41(1)
Os3−C6	1.86(4)	Os3−C7	1.81(4)
Os3−C8	1.91(5)	N1−C9	1.15(4)
N2−C11	1.41(4)		
Angles			
Os1−Os2−Os3	77.66(6)	Os2−Os1−S1	55.9(3)
Os2−Os1−N2	50.8(9)	Os2−Os1−N1	104.6(7)
Os2−Os1−C1	118(1)	Os2−Os1−C2	144(1)
S1−Os1−N1	160.4(8)	S1−Os1−N2	76.5(9)
N1−Os1−N2	90(1)	Os1−Os2−S1	51.9(2)
Os1−Os2−N2	48.0(9)	Os1−Os2−C3	80(1)
Os1−Os2−C4	137(1)	Os1−Os2−C5	125(1)
Os3−Os2−S1	55.3(3)	Os3−Os2−N2	49.4(9)
Os3−Os2−C3	151(1)	Os3−Os2−C4	90(1)
Os3−Os2−C5	109(1)	S1−Os2−N2	72.5(9)
S1−Os2−C3	120(1)	S1−Os2−C4	143(1)
S1−Os2−C5	86(1)	N2−Os2−C3	102(1)
N2−Os2−C4	93(1)	N2−Os2−C5	156(1)
Os2−Os3−S1	56.4(3)	Os2−Os3−N2	52.3(9)
Os2−Os3−C6	101(1)	Os2−Os3−C7	111(1)
Os2−Os3−C8	146(1)	S1−Os3−N2	74.6(9)
S1−Os3−C6	157(1)	S1−Os3−C7	93(1)
S1−Os3−C8	100(1)	N2−Os3−C6	91(1)
N2−Os3−C7	162(1)	N2−Os3−C8	101(1)
Os1−S1−Os2	72.2(3)	Os1−S1−Os3	94.3(3)
Os2−S1−Os3	68.3(3)	Os1−N2−Os2	81(1)
Os1−N2−Os3	110(1)	Os2−N2−Os3	78(1)
Os1−N2−C11	124(2)	Os2−N2−C11	127(2)
Os3−N2−C11	121(2)	Os1−N1−C9	171(2)
N1−C9−C10	177(3)		

In previous research, we found that the reaction of thionylaniline with either $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCMe)_2$ produced $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ as the major product, and the reactivity observed with $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(NCMe)_2$ is analogous. In addition, the chemistry of the triruthenium carbonyl clusters

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(24) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994.

with thioanaline produces a pair of Ru_4 clusters: $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}S)$ and $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}NPh)$ in low yields. It is possible that analogous high-nuclearity osmium compounds were simply not separable from the reaction mixture, but the separation procedure for the osmium complexes appeared to be highly satisfactory, so it is more likely that the difference in products results from the more robust nature of osmium clusters, which suppresses fragmentation, and subsequent cluster building, which appears to be responsible for the Ru_4 products. The more robust nature of $Os_3(CO)_{12}$ compared to $Ru_3(CO)_{12}$ is well documented in a variety of chemistries, where the ruthenium cluster is often found to fragment and to cluster-build more readily than $Os_3(CO)_{12}$. This difference is generally attributed to stronger Os−Os bonds.[25] In keeping with the more labile M−M bonds for the lighter d-block metals, our current research on the reaction of thioaniline with triiron carbonyl clusters leads to extensive cleavage of Fe−Fe bonds.

Acknowledgment. We are grateful for support of this work by the Department of Energy, Basic Energy Science Program, Grant No. DE-FG02-86ER13640. W.-Y.Y. thanks the National Science Council of Taiwan for financial support, Grant No. 33140F.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**−**3** are available on the Internet only. Access information is given on any current masthead page.

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