Synthesis and Reaction Chemistry of New, High-Oxidation-State Ruthenium and Osmium Sulfido Complexes

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An osmium sulfido complex, $[N(n\text{-}Bu)_4][Os(N)(S)(CH_2SiMe_3)_2]$, was isolated from the reaction of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with lithium sulfide. Polynuclear osmium sulfido complexes were also produced in the reaction. Osmium(VI) and ruthenium(VI) sulfido clusters, $[Y][\{M(N)R_2\}_3(\mu_3\text{-}S)_2]$ ($Y = N(n\text{-}Bu)_4$ PPh_4; M = Os, R = CH_2SiMe_3; M = Ru, R = CH_3, CH_2SiMe_3), were prepared by the reaction of $[Y][M(N)R_2Cl_2]$, $[M(N)R_2(py)_2][BF_4]$, $M(N)R_2Cl$ and Li_2S and $[Y][BF_4]$. The molecular structure of $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)_2]$ was determined by X-ray diffraction. Crystals of $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)_2]$ are in space group $P2_1/n$ with $a = 13.959(4)$ Å, $b = 30.265(11)$ Å, $c = 14.666(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 95.76(3)°$, $Z = 4$, $R = 0.044$, and $R_w = 0.040$. These sulfido complexes are stable to air and water. They react slowly with tertiary phosphines but not with other donor molecules. The neutral, S-methylated complex $\{Ru(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_3)$ is formed by reaction of $CH_3OSO_2CF_3$ with $[PPh_4]\{Ru(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)_2$. Reaction of $[Cu(NCMe)_2(PPh_3)_2][PF_6]$ with $[PPh_4][\{Ru(N)(CH_3)_2\}_3(\mu_3\text{-}S)_2]$ yields $[Cu(PPh_3)_2]\{Ru(N)(CH_3)_2\}_3(\mu\text{-}S_2)]$.

Introduction

Interest in transition-metal organometallic sulfido complexes stems from their relevance to models for metalloenzyme active sites and to catalysts for hydrodesulfurization.[1,2] A variety of sulfur-containing substrates have been used to introduce the sulfido ligand into transition metal complexes, including H_2S, S_8, RSH, Na_2S, $(Me_3Si)_2S$, CS_2, and $(CH_2CH_2)S$.[3]

Organometallic complexes containing terminal sulfido ligands are known,[1,4] but the polarizability of the S^{2-} ligand leads to the formation of many complexes with bridging sulfides.[5] Recently synthesized examples of μ_2-sulfido complexes include $[(\eta^5\text{-}C_5Me_5)M]_2(\mu_2\text{-}S)_2$ (M = Ir, Rh) and $[(\eta^5\text{-}C_5Me_5)Re(O)]_2(\mu_2\text{-}S)_2$.[6] Complexes with μ_3-sulfido ligands include clusters with a $\{M_3S_2\}$ molecular core.[7] Representative examples are $Cp_3Ni_3(\mu_3\text{-}S)_2$,[8] $[Co_3(\mu_3\text{-}S)_2(MeCp)_3]^{2+}$,[9] $M_3(\mu_3\text{-}S)_2(CO)_9$ (M = Fe, Ru, Os),[10] and $[Mn_3(\mu_3\text{-}S)_2(CO)_9]^-$.[11] Complexes with a sulfido ligand bridging four metal centers, such as $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$, $Os_6(CO)_{17}(\mu_4\text{-}S)$, and $Os_7(CO)_{19}(\mu_4\text{-}S)$, have also been prepared.[12]

One of our research goals is to prepare high-oxidation-state organometallic complexes containing reactive heteroatom ligands and to investigate atom transfer reactions between these complexes and unsaturated organic molecules. Our strategy is to synthesize a terminal sulfido complex containing another multiply bonded ligand such as a nitride in which the competition for multiple bonding orbitals would provide a driving force for the transfer of the sulfur ligand. This could be accomplished by the substitution of S^{2-} for chloride or other weakly bonded ligands in nitridoosmium(VI) and nitridoruthenium(VI) complexes.

The chloride ligands in $[N(n\text{-}Bu)_4][M(N)R_2Cl_2]$ and $[M(N)R_2Cl]_2$ (M = Ru, Os) are readily replaced by other anionic groups. We have previously synthesized the μ-oxo complexes $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2Z]$ (Z

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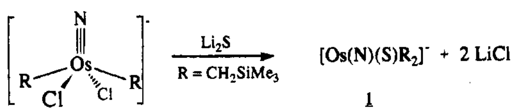
Scheme 1



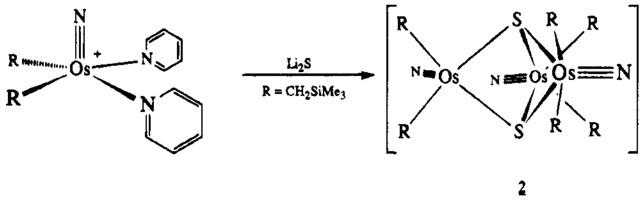
= CrO_2, MoO_2, WO_2) and $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(OReO_3)_2]$ by metathesis reactions of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with the appropriate oxoanion.[13] The analogous reaction with the tetrathiotungstate anion and $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ produced the μ-sulfido complex $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]$.[14] The complexes $[BF_4][M(N)(CH_2SiMe_3)_2L_2]$ (L= NCMe, py) are even more reactive and readily substitute L for a variety of neutral and anionic groups.[15,16] In this paper, we describe the synthesis of the nitrido sulfido complex $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2S]$ by the substitution reaction of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with Li_2S. We also present the synthesis of various 48 electron clusters $[Y][\{M(N)R_2\}_3(\mu_3\text{-}S)_2]$ (Y = $N(n\text{-}Bu)_4$, PPh_4; M = Os, R = CH_2SiMe_3; M = Ru, R = CH_3, CH_2SiMe_3), by the reactions of Li_2S with the complexes $[M(N)R_2Cl_2]^-$, $[Os(N)(CH_2SiMe_3)_2Cl]_2$, and $[M(N)(CH_2SiMe_3)_2(NC_5H_5)_2]^+$. Some preliminary reaction chemistry of the novel high-oxidation-state organometallic sulfido clusters is discussed.

Results

Synthesis of $[N(n\text{-}Bu)_4][Os(N)(S)(CH_2SiMe_3)_2]$ and $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(S)_2]$. The reaction of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with 2 equiv of lithium sulfide in tetrahydrofuran in the presence of tetramethylethanediamine (TMEDA) at room temperature produces a complex mixture of sulfur-containing organometallic products. A sulfido complex of stoichiometry $[N(n\text{-}Bu)_4][Os(N)(S)(CH_2SiMe_3)_2]$ (**1**), was isolated as yellow crystals in up to 40% yield by crystallizing the crude product mixture from methylene chloride/hexane solutions at low temperature (Scheme 1). The other sulfur-containing complexes produced in this reaction were less polar and more soluble in nonpolar organic solvents than **1**. An IR spectrum of the material remaining after crystallization of **1** did not show bands associated with terminal Os=S stretching vibrations, and the other complexes must contain only bridging sulfido ligands.

Complex **1** was characterized by ^1H NMR, IR, and mass spectroscopy and elemental analysis. The ^1H NMR spectrum shows a pair of doublets at δ 2.08 and 1.96 for the diastereotopic methylene protons and a singlet at δ 0.09 for the methyl protons of the equivalent (trimethylsilyl)methyl ligands. The infrared spectrum includes bands associated with the terminal nitrido (Os≡N) and sulfido (Os=S) ligands at 1097 and 613 cm^{-1}, respectively. A fast atom bombardment mass spectrum (FAB-MS) exhibited the M^+ peak of $[N(n\text{-}Bu)_4]^+$ (m/z 242) in the positive ion mode and the M^- peak of $[Os(N)(S)(CH_2SiMe_3)_2]^-$ (m/z 412) in the negative ion mode. The calculated pattern of isotope cluster abundance is identical with that found in the mass spectrum.

Scheme 2



One of the complexes produced in the reaction of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with lithium sulfide could be produced in high yield by another route. Addition of 2 equiv of recrystallized lithium sulfide to a methylene chloride solution of $[Os(N)(CH_2SiMe_3)_2(NC_5H_5)_2][BF_4]$ gives the triosmium sulfido cluster $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(S)_2]$ (**2**) in 80% yield (Scheme 2) Analytically pure yellow crystals of **2** are obtained from toluene/methylene chloride/hexane solution. Complex **2** can be prepared equally well from $[Os(N)(CH_2SiMe_3)_2(NCMe)_2][BF_4]$ and Li_2S. The product can also be prepared by the reaction of Li_2S with $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$, $[Os(N)(CH_2SiMe_3)_2Cl]_2$, or $Os(N)(CH_2SiMe_3)_2(NC_5H_5)Cl$ in very low to moderate yields.

Complex **2** has been completely characterized by ^1H NMR, ^{13}C NMR, IR, and mass spectroscopy, elemental analysis, electrochemistry, and X-ray crystallography. NMR spectroscopy shows that all the alkyl ligands are equivalent in this complex. The ^1H NMR spectrum of **2** in $CDCl_3$ includes two doublets at δ 2.42 and 2.04 for the diastereotopic methylene protons of the six equivalent (trimethylsilyl)methyl ligands and a singlet at δ 0.08 for the methyl protons of the alkyl ligand along with resonances of the tetra-n-butylammonium cation. Two singlets are observed in the $^{13}C\{^1H\}$ NMR spectrum at δ 4.86 and 1.01 for the methylene and methyl protons of the (trimethylsilyl)methyl ligands, along with four singlets assigned to the carbons of the cation. The IR spectrum of **2** includes bands associated with the (trimethylsilyl)methyl group and an osmium nitride stretching vibration at 1096 cm^{-1}. The fast atom bombardment mass spectrum shows the M^+ peak of the $N(n\text{-}Bu)_4$ cation at m/z 242 in the positive ion mode and the M^- peaks of $[\{Os(N)(CH_2SiMe_3)_2\}_3(S)_2]^-$ centered at m/z 1200 in the negative ion mode. A calculated simulation of the mass spectrum for $Os_3S_2N_3Si_6C_{24}H_{66}$ was identical with the pattern found at m/z 1200. The electrochemistry of **2** was examined using cyclic voltammetry and Osteryoung square-wave voltammetry. This showed a quasi-reversible oxidation at 1.2 V.

Molecular Structure of $[N(n\text{-}Bu)_4][(Os(N)(CH_2SiMe_3)_2)_3(S)_2]$. The molecular structure of complex **2** was determined by single-crystal X-ray diffraction. Bond lengths and selected bond angles are given in Table 1, an ORTEP diagram of **2** is shown in Figure 1, and the $Os_3N_3C_6S_2$ core is shown in Figure 2. The three osmium atoms and three nitrido nitrogen atoms are in a plane. The osmium atoms form an equilateral triangle and a sulfur atom caps each face. The nitrogen atoms are directed in a pinwheel fashion, giving the $Os_3N_3C_6S_2$ core C_{3h} symmetry. The two alkyl groups on each

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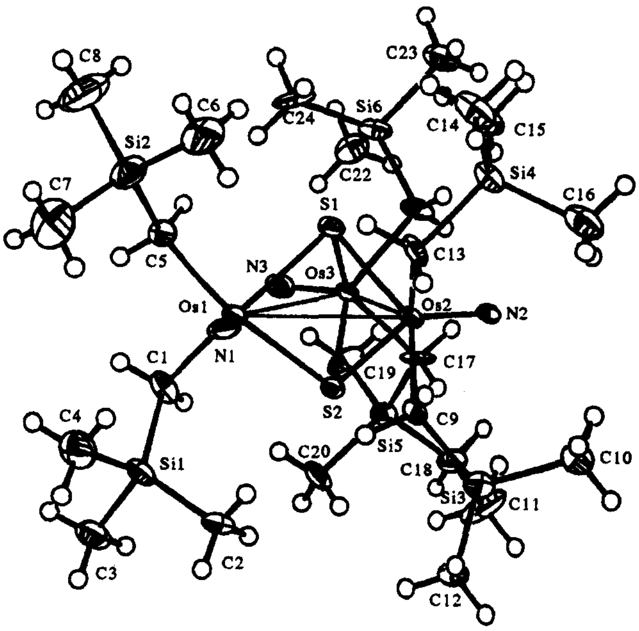


Figure 1. ORTEP diagram of **2**.

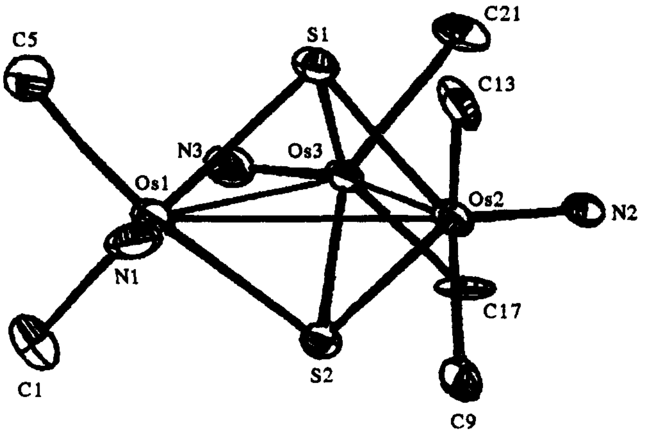


Figure 2. $Os_3N_3C_6S_2$ core of **2**.

Table 1. Selected Bond Distances and Bond Angles for 2

Distances (Å)			
Os1—Os2	3.1931(8)	Os1—N1	1.60(1)
Os1—Os3	3.2038(8)	Os2—N2	1.61(1)
Os2—Os3	3.1707(8)	Os3—N3	1.63(1)
Os1—S1	2.393(4)	Os1—C1	2.13(1)
Os1—S2	2.392(4)	Os1—C5	2.11(1)
Os2—S1	2.390(4)	Os2—C9	2.14(1)
Os2—S2	2.399(4)	Os2—C13	2.10(1)
Os3—S1	2.384(4)	Os3—C17	2.11(1)
Os3—S2	2.381(4)	Os3—C21	2.13(1)

Angles (deg)			
Os2—Os1—Os3	59.43(2)	S1—Os1—S2	79.1(1)
S1—Os1—N1	109.8(4)	N1—Os1—C1	105.6(6)
S2—Os1—N1	111.3(4)	N1—Os1—C5	106.0(6)
Os1—Os2—Os3	60.45(2)	S1—Os2—S2	79.0(1)
S1—Os2—N2	113.2(4)	N2—Os2—C9	104.6(6)
S2—Os2—N2	110.6(4)	N2—Os2—C13	105.9(5)
Os1—Os3—Os2	60.12(2)	S1—Os3—S2	79.5(1)
S1—Os3—N3	112.5(4)	N3—Os3—C17	105.6(6)
S2—Os3—N3	111.2(4)	N3—Os3—C21	105.5(6)

osmium center are in a *cis* configuration with one directed above the Os—N plane and one below this plane.

Synthesis of [Y][{Ru(N)R$_2$}$_3$(S)$_2$]. Ruthenium analogs to **2** can be prepared from bis((trimethylsilyl)methyl)(nitridoruthenium(VI) precursors (Scheme 3). When lithium sulfide is added to a solution of [Ru(N)-$(CH_2SiMe_3)_2Cl]_2$ containing either $[N(n\text{-}Bu)_4][BF_4]$ or $[PPh_4][BF_4]$, $[N(n\text{-}Bu)_4][\{Ru(N)(CH_2SiMe_3)_2\}_3S_2]$ (**3a**) or $[PPh_4][\{Ru(N)(CH_2SiMe_3)_2\}_3S_2]$ (**3b**) is produced. These complexes can be isolated as yellow-orange crystals. Reaction of the bis(nitrato) complex $[PPh_4][Ru(N)(CH_2SiMe_3)_2(NO_3)_2]$ with Li_2S also leads to the formation of **3b**. The lithium salt $[Li][\{Ru(N)(CH_2SiMe_3)_2\}_3S_2]$ (**3c**) is formed in the reaction between $[Ru(N)(CH_2SiMe_3)_2(NC_5H_5)_2][BF_4]$ and Li_2S. The sulfido complexes **3a** and **3b** can also be isolated in poorer yields from the complex mixture that results from the reaction of $[N(n\text{-}Bu)_4][Ru(N)(CH_2SiMe_3)_2Cl_2]$ or $[PPh_4][Ru(N)(CH_2SiMe_3)_2Cl_2]$ with lithium sulfide.

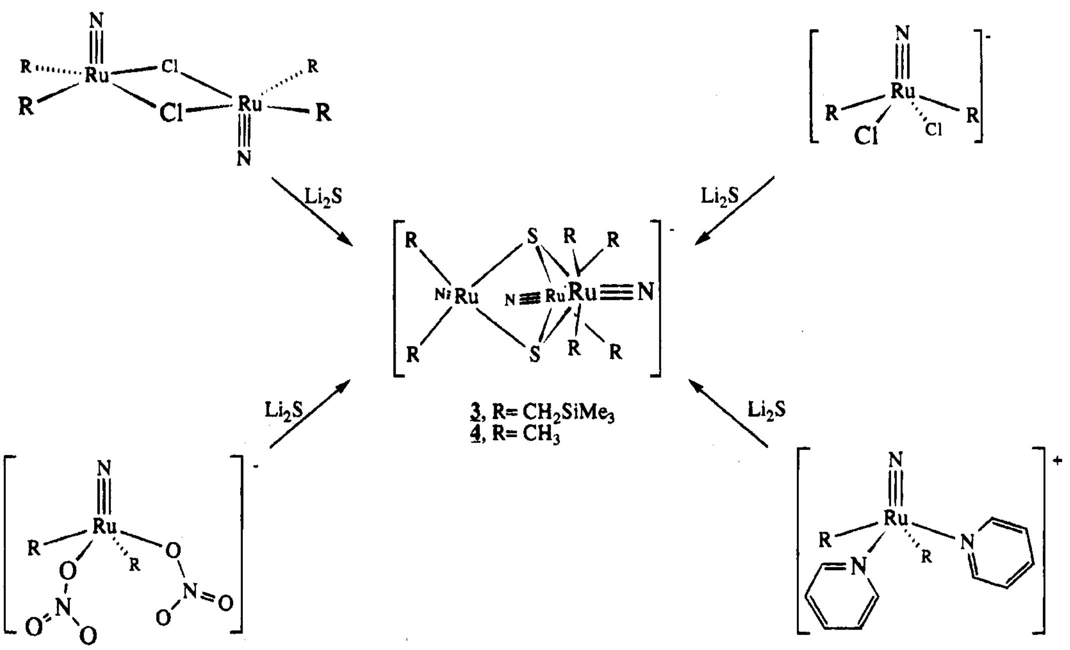
The ^1H NMR spectra of both the osmium and ruthenium clusters are similar, with a set of doublets for the diastereotopic methylene protons and a singlet for the methyl protons of the (trimethylsilyl)methyl ligands. The three salts of **3** have different solubilities, but the nature of the counterion has esentially no effect on the chemical shifts of the alkyl resonances in the NMR spectra.

Substitution of the chloride ligands in $[PPh_4][Ru(N)Me_2Cl_2]$ by Li_2S gives $[PPh_4][\{Ru(N)Me_2\}_3(S)_2]$ (**4**). The product can be isolated in 70% yield as orange crystals. Complex **4** was characterized by UV–visible, IR, and NMR spectroscopy, elemental analysis, and fast atom bombardment mass spectrometry. The infrared spectrum shows bands due to the methyl ligands and a band at 1064 cm^{-1} for the ruthenium–nitrogen stretching vibration. In the ^1H NMR spectrum of **4** are resonances for the six equivalent methyl groups of the ruthenium centers and the tetraphenyl phosphonium resonances. The ^{13}C NMR spectrum shows one resonance for the equivalent methyl carbons and four carbon resonances for the tetraphenylphosphonium cation. A fast atom bombardment mass spectrum exhibited the M^- peak of $[\{Ru(N)Me_2\}_3(S)_2]^-$ (m/z 501) in the negative ion mode. The calculated pattern of isotope cluster abundance is identical with that found in the mass spectrum.

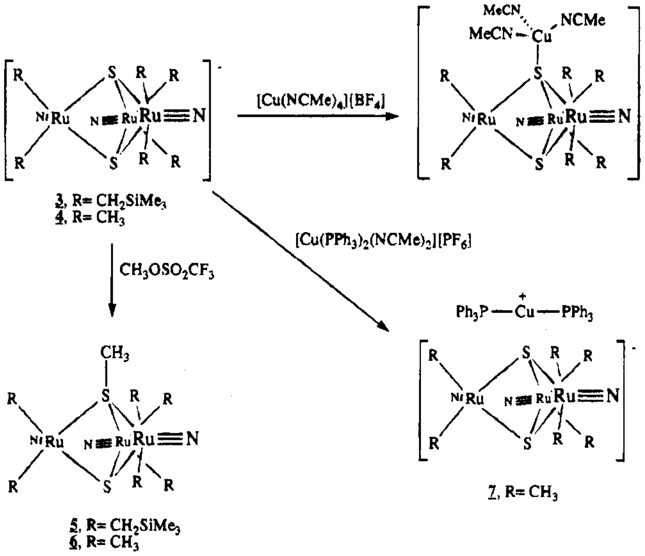
Reactivity of the Sulfido Complexes. The sulfido complexes react with PPh_3 to form $S{=}PPh_3$ and unidentified metal phosphine complexes. Complex **1** is an active sulfur transfer agent and reacts with excess PPh_3 within 30 min at room temperature to produce $S{=}PPh_3$. Complexes **2** and **4** react with triphenylphosphine much more slowly, producing low yields of $S{=}PPh_3$ after 1 day at 70 °C.

Complex **1** is moderately stable to air and water. It reacts very rapidly with protic acids and organic electrophiles. The products from these reactions have not been identified. The trinuclear sulfido complexes **2**–**4** are thermally stable and unreactive to air and water. They can be alkylated at sulfur with methyl trifluoromethanesulfonate. Complex **3b** reacts slowly with $CH_3OSO_2CF_3$ in chloroform at room temperature. After 24 h, $\{Ru(N)(CH_2SiMe_3)_2\}_3(S)(SMe)$ (**5**) can be isolated from the reaction mixture in 50% yield (Scheme 4). The product is a yellow, hexane-soluble oil. The ^1H and ^{13}C NMR spectra show that there are two sets of alkyl groups in **5** in a 1:1 ratio. The ^1H NMR spectrum shows two singlets of equal intensity for the methyl groups and four doublets for the four different diastereotopic methylene protons on the two types of (trimethylsilyl)methyl ligands. The resonance assigned to the bridging thiolate

Scheme 3



Scheme 4



methyl group is a singlet. The $^{13}C\{^1H\}$ NMR spectrum of **5** shows five resonances, one for the bridging thiolate carbon and two each for the inequivalent (trimethylsilyl)methyl ligands. The field desorption (FD) mass spectrum shows the parent peak at m/z 948, and the observed isotope pattern matches with that calculated for **5**.

The methyl complex **4** reacts completely with $CH_3OSO_2CF_3$ in 3 h at room temperature to form $\{Ru(N)Me_2\}_3(S)(SMe)$, (**6**), but the product is unstable and we have not isolated it in pure form. The ^1H NMR spectrum of **6** shows two sets of alkyl resonances at δ 2.14 and 1.87, and a singlet at δ 3.09 is attributed to the methyl protons of the bridging thiolate ligand.

Copper(I) complexes react with the triosmium and triruthenium sulfido complexes. The addition of $[Cu(NCMe)_4][BF_4]$ or $[Cu(NCMe)_4][PF_6]$ to methylene chloride solutions of **2**, **3**, or **4** results in the precipitation of orange compounds. These compounds are sparingly soluble in CH_2Cl_2, $CHCl_3$, and THF. By ^1H NMR spectroscopy, they have the formula $\{M(N)R_2\}_3S_2\{Cu(NCMe)_3\}$. The copper adducts are unstable, losing acetonitrile in solution and in the solid state to give insoluble materials. For example, complex **2** reacts with 1 equivalent of $[Cu(NCMe)_4][PF_6]$ to give $[N(n\text{-}Bu_4)][PF_6]$ and an orange product. This product has ^1H and ^{13}C NMR spectra distinct from those of **2** and so cannot be a simple salt of $[Cu(NCMe)_3][\{Os(N)(CH_2SiMe_3)_2\}_3(S)_2]$. A reasonable formulation for the product is $\{Os(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)\{\mu_3\text{-}SCu(NCMe_3)_3\}$, with the copper weakly coordinated to one of the bridging sulfido ligands. This product reverts to **2** and $[Cu(NCMe)_4][PF_6]$ with $[N(n\text{-}Bu_4)][PF_6]$ in acetonitrile solution.

Because triphenylphosphine binds more strongly to copper than does acetonitrile, we hoped we could produce a copper adduct more stable to loss of ligand by the addition of a copper(I) triphenylphosphine complex to one of the sulfido cluster complexes. Complex **4** reacts cleanly with 1 equivalent of $[Cu(NCMe)_2(PPh_3)_3][PF_6]$ in methylene chloride to give a more soluble and more stable product, $\{Ru(N)Me_2\}_3S_2Cu(PPh_3)_2$ (**7**). Complex **7** was characterized by IR and NMR spectroscopy, conductivity studies, and elemental analysis. The copper moiety may coordinate weakly to a bridging sulfide, but conductivity studies show that **7** is best represented as $[Cu(PPh_3)_2][\{Ru(N)Me_2\}_3S_2]$ in methylene chloride solution.

Discussion

We have been unable to obtain X-ray-quality single crystals of **1** for molecular structure determination, but the physical properties, reactivity, and spectroscopic data for this compound are consistent with a monomeric structure for $[N(n\text{-}Bu)_4][Os(N)(S)(CH_2SiMe_3)_2]$. The solubility of **1** in organic solvents is similar to that of other monoanionic alkylosmium complexes such as $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_4]$. We would expect a dimer or oligomer of $[\{Os(N)(S)(CH_2SiMe_3)_2\}_x]^{x-}$ to be significantly less soluble. It reacts more rapidly with PPh_3 and with $MeOSO_2CF_3$ than the trimetallic sulfido complexes **2**–**4**. Since these reagents attack the sulfido ligand, it is reasonable to expect greater reactivity for the terminal sulfido complex than for a complex with a triply bridging sulfido ligand. The negative mode FAB mass spectrum of **1** shows no osmium-containing peak with a mass/charge ratio greater than that of $[Os(N)(S)(CH_2SiMe_3)_2]^-$. This technique gives the parent ion for the trimetallic sulfides; therefore, the peak we observe for **1** is not likely to be a fragment of a larger species. A dimer, $[Os_2(N)_2(S)_2(CH_2SiMe_3)_4]^{2-}$, or a trimer, $[Os_3(N)_3(S)_3(CH_2SiMe_3)_6]^{3-}$, would have the same mass/charge ratio as a monomer but would be significantly less soluble in organic solvents. Finally, the IR spectrum of **1** is very similar to that of **2**, except that the spectrum of **1** includes a peak at 613 cm^{-1} that we assign to the $Os{=}S$ stretching vibration. While transition-metal complexes containing either a terminal nitrido or a terminal sulfido ligand are well-known, this is the first example to our knowledge of a complex containing both of these π-donor ligands.

The trimetal sulfido clusters **2**–**4** are more stable than related mononuclear organoosmium and organoruthenium complexes. Many Os(VI) and Ru(VI) nitrido alkyl species are moderately sensitive to O_2 and H_2O, especially in solution, while the sulfido clusters are robust and can be handled and kept on the benchtop. Also, while most nitrido alkyl species are hydrolyzed in attempts to purify them by column chromatography on silica gel, the sulfido clusters are stable to silica gel. The sulfido clusters are also more thermally stable than the mononuclear Ru(VI) and Os(VI) nitrido alkyl complexes.

Sulfido ligands are isoelectronic with oxo ligands but have a greater tendency to bridge metal centers due to the greater polarizability of sulfur over oxygen. The nitrido ligand is a very strong π-donor and should compete with sulfur for π symmetry orbitals on the metal center in a sulfidonitridometal complex. Enhanced reactivity due to π competition has been observed in polyoxo complexes, and π competition should increase the tendency of sulfur toward bridge bonding in sulfidonitridometal complexes.[17] In reactions between Li_2S and sources of $[Os(N)(CH_2SiMe_3)_2]^+$, we obtained **1** in variable yield (0–40%) depending on reaction conditions. In all cases, most of the osmium precursor was transformed into polynuclear complexes with bridging sulfido ligands. Under certain reaction conditions one of these clusters, **2**, formed in very high yield. Ruthenium analogs to **2** were also prepared. We were unable to isolate mononuclear ruthenium complexes with terminal sulfido ligands from these reactions.

In the absence of metal–metal bonds, each osmium center in the trimetallic complex **2** has a distorted-square-pyramidal structure very similar to those of the other structurally characterized, 5-coordinate organoosmium(VI) complexes.[18] The osmium–nitrogen distances in **2** are quite similar to the Os–N distances in other nitridoosmium(VI) complexes: $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2WS_4]$, 1.62(1) Å;[14] $[Os(N)(CH_2SiMe_3)_2(SNC_2H_4)]_2$,[19] 1.62(1) and 1.64(1) Å; $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_4]$, 1.631(1) Å.[20] The closest structural analog to **2** is $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]$. The average bond angles in the tetrathiotungstate complex are very similar: C–Os–N, 102°; S–Os–N, 108°. The S–Os–N angles are greater than the C–Os–N angles in both complexes due to electronic repulsion between the lone pair on the nitrido ligand and the lone pairs on the sulfur. The average Os–S bond length in the tetrathiotungstate complex (2.346 Å) is only slightly shorter than the average Os–S distance in **2** (2.39 Å), suggesting that there is little distortion due to sterics in the sulfido cluster. The Os–S bond lengths of **2** are within the range reported for sulfido–capped triosmium carbonyl clusters, 2.285–2.476 Å.

Trinuclear metal clusters with 48-electron cluster cores, such as $[(C_5H_4Me)_3Co_3(\mu_3\text{-}S)_2]^{2+}$ and $[Mn_3S_2(CO)_9]^-$, have metal–metal bonds between all adjacent metals.[21] The trimetallic clusters $[Cp_3Ni_3(\mu_3\text{-}S)_2]^n$ and $[(C_5H_4Me)_3Co_3(\mu_3\text{-}S)_2]^n$ (n = 0, 1+) with electron counts greater than 48 have only weak metal-metal bonds.[22] The alkylidyne clusters $(CpM)_3(CPh)_2$ (M = Rh, Ir), like the sulfido clusters, consist of a triangular array of metal atoms, capped on both faces by μ_3-alkylidyne units. A theoretical study of $(CpCo)_3(CH)_2$ showed that this molecule should have partial metal–metal bonds.[23] The carborane $(RB)_3(CR')_2$ has no boron–boron bonds, because boron has only six electrons and two are used to bond to each carbon. The osmium and ruthenium sulfido clusters $[\{M(N)R_2\}_3(S)_2]^-$ (anions of **2**–**4**) have electron counts of 48 and should have some metal–metal bonding interaction.

The Os–Os distances in **2** ($Os\text{–}Os_{av}$ = 3.19 Å) are within the Van der Waals radii but are somewhat greater than the Os–Os bond distances observed in low-oxidation-state triosmium sulfur clusters (2.75 and 2.93 Å). The osmium center has atomic orbitals of the right symmetry and an electron pair available for metal–metal bonding.[24] After forming bonds to the terminal

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nitride, two alkyls, and both bridging sulfides, osmium has an electron pair localized in the d_{xy} orbital. The d_{xz} and d_{yz} orbitals are degenerate and empty. They are antibonding with respect to the Os—N π bonds. Higher in energy are the d_{z^2} and $d_{x^2-y^2}$ orbitals, which are antibonding with respect to the ligands in the square-pyramidal array.[25] There is probably some weak metal bonding in **2**, but we do not see strong metal–metal bonds, because forming these bonds would cause electrons to occupy the d_{xz} or d_{yz} orbitals and would weaken the Os—N π bonds.

The μ_3-sulfido ligands are sufficiently electron-rich to be susceptible to electrophilic attack. The ruthenium complexes **3** and **4** react with $CH_3OSO_2CF_3$ to form products in which a sulfide has been methylated. Reactions in which μ_3-sulfido ligands in metal clusters react with carbon electrophiles to form bridging thiolate species are also well-known.[26] While complete structural characterizations of **5** and **6** have not been obtained, there is overwhelming evidence for their assignment as bridging thiolate species. NMR spectroscopy of **5** and **6** shows two sets of alkyl resonances. This is the result expected for methylation of one sulfur. Electrophiles can react with the nitrido ligand in certain Os(VI) and Ru(VI) complexes to form imides, but nitrogen methylation cannot form **5** and **6**.[27] If a methyl imide were formed at one of the nitrogens, there would be three sets of alkyl resonances instead of two. The remaining sulfido ligand in the neutral complex **5** is less electron-rich than the anionic complex **3** and does not react with excess methyl trifluoromethanesulfonate.

Alkylation of a sulfido ligand reduces the stability of the trimetal cluster. Complex **5** is significantly less stable than **3** and decomposes slowly at room temperature. Complex **6** cannot be isolated in pure form due to extensive decomposition during workup at room temperature.

The sulfido cluster complexes **2**–**4** react with $[Cu(NCMe)_4][BF_4]$ to produce 1 equivalent of free acetonitrile and sparingly soluble copper adducts. The chemical shift of the alkyl resonances on each of the trimetal sulfido clusters is shifted from those in the starting complex in the ^1H NMR, but the alkyl groups remain equivalent at room temperature. We prepared three derivatives of **3** with Li^+, PPh_4^+, and $N(n\text{-}Bu)_4^+$ cations to show that changes in counterion do not affect the position of the alkyl resonances in the ^1H NMR. A reasonable explanation for the observed change in the NMR is that $[Cu(NCMe)_3]^+$ coordinates weakly to one of the bridging sulfido ligands in each of the cluster complexes. Rapid dissociation/association of the copper and sulfido group at room temperature would lead to equivalence of the alkyl signals. Additional acetonitrile is lost from the adduct over time, and the resulting material is insoluble in organic solvents. Loss of ligand from the copper adduct $\{M(N)R_2\}_3(\mu_3\text{-}S)(\mu_4\text{-}S)Cu(NCMe)_3$ could lead to the formation of a copper-bridged polymeric material such as $[\{M(N)R_2\}_3(\mu_4\text{-}S)_2Cu(NCMe)_x]_n$. Copper(I) coordination to transition-metal clusters and transition-metal sulfides has been reported.[28] There is also precedence for the coordination of an electron-deficient $W(CO)_5$ fragment to the bridging sulfur atom of low-oxidation-state triosmium and triiron μ_3-sulfido clusters.[29]

The copper phosphine complex $[Cu(NCMe)_2(PPh_3)_2][PF_6]$ loses 2 equiv of acetonitrile upon reaction with **4** and forms a product of stoichiometry $Cu(PPh_3)_2\{Ru(N)Me_2\}_3S_2$. This material is thermally stable because the copper does not dissociate the more basic triphenylphosphine ligand, but the presence of the phosphine ligands on the Cu(I) center makes that metal a weaker Lewis acid and reduces its ability to coordinate the bridging sulfido ligand. ^1H NMR, ^{13}C NMR, and conductivity studies show that **7** is a salt, $[Cu(PPh_3)_2][\{Ru(N)Me_2\}_3(\mu_3\text{-}S)_2]$. Steric repulsions between the relatively bulky triphenylphosphine ligands on the copper and the sulfido cluster may force the complex to dissociate in solution into an ionic species. Osmometry studies of Cu(I) species have shown that they are prone to dissociate in solution to avoid steric congestion around the metal center.[30]

Conclusion

High-oxidation-state sulfur-containing osmium and ruthenium complexes have been prepared. A complex with stoichiometry $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(S)]$ can be prepared in low to moderate yields by reaction of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with lithium sulfide, but stable trimetallic clusters are the major products in all reactions of $[M(N)R_2Cl_2]^-$ and $[M(N)R_2L_2]^+$ with S^{2-}. An X-ray structure analysis of one of these clusters, **2**, shows that the two sulfur ligands cap the two faces of a triangular osmium base with each metal center having a slightly distorted square pyramidal geometry. The structure of **2** has bond angles and distances comparable to those of $[N(n\text{-}Bu)4][Os(N)(CH_2SiMe_3)_2WS_4]$. These complexes are stable to air and water and are also thermally stable. While there may be weak metal–metal bonding in **2**, bonding between the metal centers and the terminal nitrido ligands is more significant. The triply bridging sulfur atoms of **2**–**4** remain electron rich. These complexes also react with methyl trifluoromethanesulfonate at one of the bridging sulfurs to yield S-methylated μ_3-methanethiolate complexes.

Experimental Section

All reactions were done under nitrogen atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres glovebox unless otherwise stated. Anhydrous ether, THF, and hexane were distilled from Na/benzophenone. Methylene chloride and acetonitrile were distilled from CaH_2. Toluene was distilled from Na. Deuterated chloroform was distilled from CaH_2 and dried over molecular sieves. Lithium sulfide was purchased from Aldrich and was recrystallized from absolute ethanol/diethyl ether under nitrogen. $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$,[20] $[NOs(CH_2SiMe_3)_2(NC_5H_5)_2][BF_4]$, $[PPh_4]$-

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$[Ru(N)(CH_2SiMe_3)_2(NO_3)_2]$,[16] $[PPh_4][Ru(N)(CH_3)_2Cl_2]$,[31] $[Ru(N)(CH_2SiMe_3)_2(NC_5H_5)_2]$, $[\{Ru(N)(CH_2SiMe_3)_2Cl\}_2]$,[16] and $Cu(NCCH_3)_2(PPh_3)_2PF_6$[32] were prepared according to literature methods.

NMR spectra were recorded on Varian XL-200, GE QE-300, Varian Unity-400, and GE GN-500 FT NMR spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a VG ZAB-SE (FAB) or Finnigan-Mat 731 (FD). All analyses were performed by the University of Illinois microanalytical service. UV–visible spectra were obtained on a Hewlett- Packard 8452A diode array spectrophotometer.

Electrochemical measurements were made with a BAS 100 electrochemical analyzer. All electrochemistry was done in a Vacuum Atmospheres drybox. Measurements were taken on approximately 0.01 M solutions of the compound of interest by using $[N(n\text{-}Bu)_4][BF_4]$ as the supporting electrolyte. A platinum-disk microelectrode and a platinum wire were used as the working and auxiliary electrodes, respectively. An Ag/AgCl aqueous reference microelectrode was used. Solutions of 0.1 M $[N(n\text{-}Bu)_4][BF_4]$ in acetonitrile were prepared from freshly distilled solvent. Potentials are reported vs SCE after calibration with the ferrocene/ferrocenium couple.

Preparation of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiCH_3)_2(S)]$ (1). A solution of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.04 g, 0.058 mmol) was added to a suspension of Li_2S (0.027 g, 0.58 mmol) in 30 mL of CH_2Cl_2, and the mixture was magnetically stirred at room temperature. The color gradually changed from orange to yellow. After 24 h, the mixture was filtered and solvent was removed from the filtrate under vacuum. The residue was crystallized from hexane/CH_2Cl_2 at −30 °C. Yellow crystals were collected (0.015 g, 40%) and dried under vacuum. IR (KBr, cm^{-1}): 2961–2878 (s, ν_{CH}), 1466 (m, δ_{CH}), 1240 (s, δ_{SiC}), 1097 (s, ν_{OsN}), 852 (s, ν_{SiC}), 831 (s, ν_{SiC}), 613 (m, ν_{Os-S}). ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 3.25 (m, 4 H, NCH_2), 2.08 (d, J = 10 Hz, 1 H, $OsCH^aH^b$), 1.96 (d, J = 10 Hz, 1 H, $OsCH^aH^b$), 1.61 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.42 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, J = 7 Hz, 6 H, $NCH_2CH_2CH_2CH_3$), 0.09 (s, 9 H, $SiCH_3$). Anal. Calcd for $OsSN_2Si_2C_{24}H_{58}$: C, 44.13; H, 8.95; N, 4.29. Found: C, 43.91; H, 9.04; N, 3.95. Mass spectrum (FAB, 3:1 dithiothreitol/dithioerythritol, m/z): 412, (M^-, $[Os(N)(CH_2SiCH_3)_2(S)]^-$, 20%), 242 ($M^+$, $[NBu_4]$, 100%).

Preparation of $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)_2]$ (2). A solution of $[Os(N)(CH_2SiMe_3)_2(py)_2][BF_4]$ (0.030 g, 0.048 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a suspension of Li_2S (0.002 mg, 0.043 mmol) and $[N(n\text{-}Bu)_4][BF_4]$ (0.005 g, 0.015 mmol) in 5 mL of CH_2Cl_2. The solution changed from yellow to orange and then slowly returned to yellow. The reaction mixture was stirred for 2 h, and then the yellow solution was filtered through Celite. The solvent was removed from the filtrate under vacuum. The residue was dissolved in diethyl ether, hexane was added, and the solution was concentrated to produce microcrystals of **2**. The product was recrystallized from toluene/CH_2Cl_2/hexane at −30 °C to give yellow crystals of **2** (0.020 g, 0.014 mmol, 87%). IR (KBr pellet, cm^{-1}): 2961 (s, ν_{CH}), 2893 (s, ν_{CH}), 2853 (s, ν_{CH}), 1481 (m, δ_{CH}), 1463 (m, δ_{CH}), 1252 (s, δ_{SiC}), 1240 (s, δ_{SiC}), 1096 (s, ν_{OsN}), 853 (s, ν_{SiC}), 830 (s, ν_{SiC}). ^1H NMR (300 MHz, $CDCl_3$, 19 °C): δ 3.24 (t, J = 8 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 2.42 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 2.04 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 1.61 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.43 (sextet, J = 7.2 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, J = 7.2 Hz, 6 H, $NCH_2CH_2CH_2CH_3$), 0.082 (s, 27 H, $SiCH_3$). ^1H NMR (300 MHz, CD_2Cl_2, 19 °C): δ 3.04 (t, J = 8 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 2.36 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 2.00 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 1.58 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.43 (sextet, J = 7.2 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 1.03 (t, J = 7.2 Hz, 6 H, $NCH_2CH_2CH_2CH_3$), 0.085 (s, 27 H, $SiCH_3$). ^1H NMR (300 MHz, CD_3CN, 19 °C): δ 3.06 (t, J = 8 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 2.32 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 1.98 (d, J = 10.5 Hz, 3 H, $OsCH^aH^b$), 1.58 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.33 (sextet, J = 7.2 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, J = 7.2 Hz, 6 H, $NCH_2CH_2CH_2CH_3$), 0.07 (s, 27 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 19.4 °C): δ 58.82 ($NCH_2CH_2CH_2CH_3$), 24.11 ($NCH_2CH_2CH_2CH_3$), 19.80 ($NCH_2CH_2CH_2CH_3$), 13.73 ($NCH_2CH_2CH_2CH_3$), 4.86 ($OsCH_2$), 1.01 ($SiCH_3$). Mass spectrum (FAB, 3-NBA and Magic Bullet, m/z): 1200 (M^-, $[(Os(N)(CH_2SiMe_3)_2)_3S_2]$); 242 ($M^+$, $[N(C_4H_9)_4]$). Anal. Calcd. for $Os_3C_{40}H_{102}N_4Si_6S_2$: C, 33.31; H, 7.13; N, 3.88. Found: C, 33.05; H, 7.19; N, 3.68.

Table 2. Crystal Data Collection and Refinement Parameters

compd	**2**
formula	$C_{40}H_{102}N_4Si_6S_2Os_3$
fw	1442.52
space group	$P2_1/n$
a, Å	13.959(4)
b, Å	30.265(11)
c, Å	14.666(5)
$\alpha = \gamma$, deg	90
β, deg	95.76(3)
formula/unit cell, Z	4
calcd density, (ϱ), g/cm^3	1.554
temp, °C	−75
radiation	Mo Kα (graphite crystal monochromator); Kα_1 = 0.70930 Å, Kα_2 = 0.713 59 Å, Kα = 0.710 73 Å
abs coeff (μ), cm^{-1}	63.81
R^a	0.044
$R_w{}^b$	0.040

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

Molecular Structure of 2. The transparent, yellow, equidimensional data crystal had mostly well-developed faces and uniformly extinguished plane-polarized light. All of the crystals examined were slightly twinned and had a broad reflection scan width. The data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber and then cooled to −75 °C with the (186) scattering planes roughly normal to the spindle axis.

The structure was solved by Patterson methods (SHELXS-86); correct positions for the three osmium atoms were deduced from a vector map, and partial structure expansion revealed positions for the sulfur and silicon atoms. Subsequent least-squares refinements and difference Fourier syntheses gave positions for the remaining non-H atoms, including disordered positions for atom C36. Ordered H atoms were included as fixed contributors in "idealized" positions. In the final cycle of least-squares refinement, common isotropic thermal parameters were refined for hydrogen atoms and the disordered C atom, a relative site occupancy factor was varied for atom C36, and anisotropic thermal coefficients were refined for the ordered non-H atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. The highest residual electron density peaks in the final difference Fourier map were in the vicinity of the osmium atoms. A final analysis of variance between observed and calculated structure factors failed to identify any systematic errors.

$[N(n\text{-}Bu)_4][\{Ru(N)(CH_2SiMe_3)_2\}_3S_2]$ (3a). Finely ground Li_2S (0.003 g, 0.06 mmol) was added to a solution of $[Ru(N)(CH_2SiMe_3)_2Cl]_2$ (0.039 g, 0.062 mmol) and $[N(n\text{-}Bu)_4][BF_4]$ (0.020 g, 0.062 mmol) in 5 mL of CH_3CN. The reaction mixture was stirred for 10 h during which time the orange solution became yellow. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The yellow residue was dissolved in diethyl ether. Hexane was added until the solution became cloudy. Cooling the solution to −30 °C afforded **3a** (0.010 g, 0.009 mmol, 22%) as orange crystals. ^1H NMR (500 MHz, $CDCl_3$, 19.7 °C): δ 2.96 (t, J = 8 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 1.78 (d, J = 10.5 Hz, 3 H, $RuCH^aH^b$), 1.52

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(m, 4 H, $\mathrm{NCH_2}CH_2\mathrm{CH_2CH_3}$), 1.43 (sextet, $J = 7$ Hz; 4 H, $\mathrm{NCH_2CH_2}CH_2\mathrm{CH_3}$), 1.32 (d, $J = 10.5$ Hz, 3 H, $\mathrm{RuCH^a}H^b$), 1.03 (t, $J = 7$ Hz, 6 H, $\mathrm{NCH_2CH_2CH_2}CH_3$), 0.10 (s, 27 H, $\mathrm{SiCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125 MHz, $\mathrm{CDCl_3}$, 18.8 °C): δ 58.62 ($\mathrm{NCH_2CH_2CH_2CH_3}$), 23.99 ($\mathrm{NCH_2CH_2CH_2CH_3}$), 19.82 ($\mathrm{NCH_2CH_2CH_2CH_3}$), 13.71 ($\mathrm{NCH_2CH_2CH_2CH_3}$), 11.75 ($\mathrm{RuCH_2}$), 1.39 ($\mathrm{SiCH_3}$). IR (KBr pellet, $\mathrm{cm^{-1}}$): 2949–2868 (m, ν_{CH}), 1480 (w, δ_{CH}), 1240 (m, δ_{SiC}), 1061 (m, ν_{RuN}), 851 (s, γ_{SiC}), 828 (s, ν_{SiC}). Mass spectrum (FAB, m/z): 932 ($\mathrm{M^-}$, $[(\mathrm{Ru(N)(CH_2SiMe_3)_2})_3\mathrm{S_2}]$), 242 ($\mathrm{M^+}$, $[\mathrm{N(C_4H_9)_4}]$). Anal. Calcd for $\mathrm{C_{40}H_{102}N_4Si_6S_2Ru_3}$: C, 40.88; H, 8.75; N, 4.77. Found: C, 41.06; H, 8.73; N, 4.65.

$[\mathrm{PPh_4}][\{\mathrm{Ru(N)(CH_2SiMe_3)_2}\}_3\mathrm{S_2}]$ (3b). Solid $\mathrm{Li_2S}$ (0.002 g, 0.044 mmol) was added to a solution of $[\mathrm{PPh_4}][\mathrm{Ru(N)(CH_2SiMe_3)_2(NO_3)_2}]$ (0.042 g, 0.056 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$. The orange solution became yellow-orange immediately upon addition of the $\mathrm{Li_2S}$. The reaction mixture was stirred for 12 h and then filtered through Celite to remove the LiCl. The solvent was removed from the filtrate under reduced pressure, and the yellow residue was dissolved in diethyl ether. The solution was cooled to −30 °C and hexane added until the solution became cloudy. A few drops of $\mathrm{CH_2Cl_2}$ were added to the cold solution, and the solution was recooled to −30 °C. Yellow crystals of **3b** (0.018 g, 0.014 mmol, 76%) were collected by filtration and dried under vacuum. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 19.7 °C): δ 7.92 (m, 2 H, p-$\mathrm{PC_6}H_5$), 7.77 (m, 4 H, o-$\mathrm{PC_6}H_5$), 7.60 (m, 4 H, m-$\mathrm{PC_6}H_5$), 1.77 (d, $J = 10.6$ Hz, 3 H, $\mathrm{RuC}H^a\mathrm{H^b}$), 1.33 (d, $J = 10.6$ Hz, 3 H, $\mathrm{RuCH^a}H^b$), 0.07 (s, 27 H, $\mathrm{SiMe_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (75 MHz, $\mathrm{CDCl_3}$, 18 °C): δ 136.05 (d, $J = 3$ Hz, p-$\mathrm{P}C_6\mathrm{H_5}$), 134.72 (d, $J = 10$ Hz, o-$\mathrm{P}C_6\mathrm{H_5}$), 130.88 (d, $J = 13$ Hz, m-$\mathrm{P}C_6\mathrm{H_5}$), 117.30 (d, $ipso$-$\mathrm{P}C_6\mathrm{H_5}$), 11.25 (s, $\mathrm{RuCh_2}$), 1.34 (s, $\mathrm{SiCH_3}$). IR (KBr pellet, $\mathrm{cm^{-1}}$) 3058–2869 (s, ν_{CH}), 1438 (m, ν_{CC}), 1239 (s, δ_{SiC}), 1109 (s, $\delta(\mathrm{ip})_{\mathrm{CH}}$), 1065 (s, ν_{RuN}), 851 (s, γ_{SiC}), 828 (s, ν_{SiC}), 527 (s, $\delta(\mathrm{oop})_{\mathrm{CH}}$). Anal. Calcd for $\mathrm{RuC_{48}H_{86}N_3Si_6PS_2}$: C, 45.32; H, 6.81; N, 3.30. Found: C, 44.14; H, 6.70; N, 3.11. Electrochemistry: irreversible oxidations at +0.92 and +1.50 V were found at 5120 mV/s.

$[\mathrm{Li}][\{\mathrm{Ru(N)(CH_2SiMe_3)_2}\}_3\mathrm{S_2}]$ (3c). Solid $\mathrm{Li_2S}$ (0.003 g, 0.062 mmol) was added to a solution of $[\mathrm{Ru(N)(CH_2SiMe_3)_2(NC_5H_5)_2}]$ (0.035 g, 0.062 mmol) in 5 mL of $\mathrm{CH_3CN}$. The solution became lighter orange upon addition of the $\mathrm{Li_2S}$. The mixture was stirred for 10 h and filtered to remove the LiCl. The solvent was removed from the filtrate under reduced pressure, and a ^{1}H NMR spectrum of the residue was obtained. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 19.7 °C): δ 1.78 (d, $J = 11.4$ Hz, 1 H, $\mathrm{RuC}H^a\mathrm{H^b}$), 1.34 (d, $J = 11.4$ Hz, 1 H, $\mathrm{RuCH^a}H^b$), 0.09 (s, 9 H, $\mathrm{SiCH_3}$).

Preparation of $[\mathrm{PPh_4}][\{\mathrm{Ru(N)(CH_3)_2}\}_3\mathrm{S_2}]$ (4). $\mathrm{Li_2S}$ (0.003 g, 0.060 mmol) was added all at once to an orange solution of $[\mathrm{PPh_4}][\mathrm{Ru(N)(CH_3)_2Cl_2}]$ (0.050 g, 0.090 mmol) in 25 mL of $\mathrm{CH_2Cl_2}$, and the mixture was magnetically stirred at room temperature. The solution changed slowly to yellow. After 12 h, the solution was filtered through Celite to remove LiCl. The solvent was removed under vacuum from the filtrate, and the yellow residue was redissolved in ~1:1 THF/diethyl ether and filtered through Celite to remove $\mathrm{PPh_4Cl}$. Solvent was removed from the filtrate under vacuum, and the residue was crystallized from $\mathrm{CH_2Cl_2}$/hexane at −30 °C. Compound **4**, a dark orange crystalline solid (0.018 g, 0.021 mmol, 71.5%), was collected by filtration. IR (KBr pellet, $\mathrm{cm^{-1}}$): 3060–2772 (s, ν_{CH}), 1585 (m, $\nu_{\mathrm{C=C}}$), 1483 (s, δ_{CH}), 1435 (vs, $\nu_{\mathrm{C=C}}$), 1064 (s, ν_{RuN}), 753 (vs, δ_{CH}), 723 (vs, δ_{CH}), 687 (vs, δ_{CH}), 526 (vs, δ_{CH}). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 18 °C): δ 7.92 (m, 2 H, p-$\mathrm{PC_6H_5}$), 7.77 (m, 4 H, o-$\mathrm{PC_6H_5}$), 7.60 (m, 4 H, m-$\mathrm{PC_6H_5}$), 1.55 (s, 9 H, $\mathrm{RuCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$, 19 °C): δ 135.75 (d, $J = 3.1$ Hz, p-$\mathrm{C_6H_5}$), 134.24 (d, $J = 10.6$ Hz, m-$\mathrm{PC_6H_5}$), 130.69 (d, $J = 12.9$ Hz, o-$\mathrm{PC_6H_5}$), 117.22 (d, $J = 88.8$ Hz, $ipso$-$\mathrm{PC_6H_5}$), 0.39 (s, $\mathrm{RuCH_3}$). Mass spectrum (FAB, 3-NBA, negative ion, m/z): 501 ($\mathrm{M^-}$, $[\{\mathrm{Ru(N)Me_2}\}(\mathrm{S})_2]^-$); calculated isotope pattern matches pattern found. UV–visible spectrum ($\mathrm{CH_2Cl_2}$; $\lambda_{\max}$, nm (ϵ)): 236 (35 828), 266 (10 467), 330 (5784). Anal. Calcd for $\mathrm{C_{30}H_{38}N_3PS_2Ru_3}$: C, 42.95; H, 4.57; N, 5.01. Found: C, 43.28; H, 4.73, N, 5.00.

Synthesis of $\{\mathrm{Ru(N)(CH_2SiMe_3)_2}\}_3(\mu_3\text{-}\mathrm{SMe})(\mu_3\text{-}\mathrm{S})]$ (5). Yellow crystals of $[\mathrm{PPh_4}][(\mathrm{Ru(N)(CH_2SiMe_3)_2})_3\mathrm{S_2}]$ (0.005 g, 0.004 mmol) were dissolved in 0.75 mL of $\mathrm{CDCl_3}$ in a 5 mm NMR tube. $\mathrm{CH_3OSO_2CF_3}$ (2 drops, excess) was added to the solution, and the NMR tube was capped. ^{1}H NMR spectra of the sample were taken over a 24-h period until no starting material remained. After 24 h, the solvent and excess $\mathrm{CH_3OSO_2CF_3}$ were removed under vacuum. The orange solid residue was extracted with hexane and filtered through Celite to remove white solid $[\mathrm{PPh_4}][\mathrm{OSO_2CF_3}]$. Solvent was removed under vacuum, and the product was isolated as a light yellow oil (0.002 g, 0.002 mmol, 50%). IR (KBr pellet, $\mathrm{cm^{-1}}$): 2954 (m, ν_{CH}), 2916 (m, ν_{CH}), 2877 (w, ν_{CH}), 2846 (w, ν_{CH}), 1254 (vs, δ_{SiC}) 1239 (vs, δ_{SiC}), 1069 (vs, ν_{RuN}), 1015 (vs, δ_{CH}), 946 (m, ν_{SC}), 854 (vs, γ_{SiC}), 823 (vs, ν_{SiC}), 677 (w, δ_{SC}). ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$, 18.4 °C): δ 2.88 (s, 1 H, $\mathrm{SCH_3}$), 2.05(d, $J = 7.25$ Hz, 1 H, $\mathrm{RuC}H^a\mathrm{H^b}$), 1.99 (d, $J = 7.00$ Hz, 1 H, $\mathrm{RuCH^a}H^b$), 1.82 (d, $J = 6.25$ Hz, 1 H, $\mathrm{RuC}H^c\mathrm{H^d}$), 1.73 (d, $J = 6.00$ Hz, 1 H, $\mathrm{RuCH^c}H^d$), 0.125 (s, 9 H, $\mathrm{SiCH_3}$), 0.115 (s, 9 H, $\mathrm{SiCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$, 20 °C) δ 29.71 (s, $\mathrm{SCH_3}$), 17.56 (s, $\mathrm{RuCH_2}$), 15.93 (s, $\mathrm{RuCH_2}$), 0.86 (s, $\mathrm{SiCH_3}$), 0.81 (s, $\mathrm{SiCH_3}$). Mass spectrum (FD, m/z): 948.1 ($\mathrm{M^+}$). The isotope pattern of the observed mass spectrum was identical to the calculated spectrum.

Synthesis of $\{\mathrm{Ru(N)(CH_3)_2}\}_3(\mu_3\text{-}\mathrm{SMe})(\mu_3\text{-}\mathrm{S})]$ (6). Orange crystals of $[\mathrm{PPh_4}][\{\mathrm{Ru(N)Me_2}\}_3\mathrm{S_2}]$ (0.010 g, 0.012 mmol) were placed into an NMR tube and dissolved in 0.75 mL of $\mathrm{CDCl_3}$. $\mathrm{CH_3OSO_2CF_3}$ (0.001 96 g, 1.35 μL, 0.012 mmol) was added to the solution via syringe, and the NMR tube was capped with a rubber septum. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 18.0 °C): δ 3.09 (s, 1 H, $\mathrm{SCH_3}$), 2.14 (s, 3 H, $\mathrm{RuCH_3}$), 1.87 (s, 3 H, $\mathrm{RuCH_3}$).

Reaction of 2 with $\mathrm{Cu(NCMe)_4PF_6}$. $[\mathrm{N}(n\text{-}\mathrm{Bu})_4][\{\mathrm{Os(N)(CH_2SiMe_3)_2}\}_3\mathrm{S_2}]$ (0.007 g, 0.005 mmol) was dissolved in 0.75 mL of $\mathrm{CD_2Cl_2}$ and added to a 5 mm NMR tube. An initial ^{1}H NMR spectrum showed pure **2**. A $\mathrm{CD_2Cl_2}$ solution of $[\mathrm{Cu(NCMe)_4}][\mathrm{PF_6}]$ (0.181 mL, 0.0268 M, 0.005 mmol) was added. The solution changed from yellow to orange, and a ^{1}H NMR spectrum was obtained. Orange solid precipitated slowly from solution. The solid was redissolved in $\mathrm{CD_2Cl_2}$, and a ^{1}H NMR spectrum was obtained. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 19 °C): 2.75 (d, $J = 10.4$ Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^b}$), 2.45 (d, $J = 10.4$ Hz, 2 H, $\mathrm{OsCH^a}H^b$), 2.04 (s, 3 H, NCMe), 0.085 (s, 18 H, $\mathrm{SiCH_3}$). The two $\mathrm{CD_2Cl_2}$ solutions were combined, the solvent was removed under vacuum, and the orange residue was dissolved in 0.75 mL of $\mathrm{CD_3CN}$. The solution was yellow and homogeneous. ^{1}H NMR showed **2** and $\mathrm{CH_3CN}$. ^{1}H NMR (300 MHz, $\mathrm{CD_3CN}$, 19 °C): δ 3.06 (t, $J = 8$ Hz, 4 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 2.32 (d, $J = 10.5$ Hz, 3 H, $\mathrm{OsC}H^a\mathrm{H^b}$), 1.98 (d, $J = 10.5$ Hz, 3 H, $\mathrm{OsCH^a}H^b$), 1.95 (s, 5 H, $\mathrm{CH_3CN}$), 1.58 (m, 4 H, $\mathrm{NCH_2}CH_2\mathrm{CH_2CH_3}$), 1.33 (sextet, $J = 7.2$ Hz, 4 H, $\mathrm{NCH_2CH_2}CH_2\mathrm{CH_3}$), 0.99 (t, $J = 7.2$ Hz, 6 H, $\mathrm{NCH_2CH_2CH_2}CH_3$), 0.07 (s, 27 H, $\mathrm{SiCH_3}$).

Reaction of 3b with $\mathrm{Cu(NCMe)_4BF_4}$. $[\mathrm{PPh_4}][\{\mathrm{Ru(N)(CH_2SiMe_3)_2}\}_3\mathrm{S_2}]$ (0.016 g, 0.013 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ to give a yellow solution. $\mathrm{Cu(NCCH_3)_4BF_4}$ (0.004 g, 0.013 mmol) was added and the color changed to orange. The orange solution was stirred for 30 min, and the solvent was removed under reduced pressure. The residue was extracted with diethyl ether and filtered to remove $\mathrm{PPh_4BF_4}$. The solvent was removed under reduced pressure, yielding an orange solid (0.008 g, 55%). IR (KBr pellet, $\mathrm{cm^{-1}}$): 2940 (vs, $\mathrm{v_{CH}}$), 2892 (s, $\mathrm{v_{CH}}$), 2317 (m, $\mathrm{v_{NC}}$), 2286 (m , $\mathrm{v_{NC}}$), 1450 (m, $\mathrm{v_{C=C}}$), 1244 (vs, δ_{SiC}), 1064 (s, $\mathrm{v_{RuN}}$), 831 (vs, $\mathrm{v_{SiC}}$), 711 (m, δ_{CH}). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, 18 °C): δ 2.22 (s, 9 H, $CH_3\mathrm{CNCu}$), 1.99 (d, $J = 10.2$ Hz, 6 H, $\mathrm{RuC}H^a\mathrm{H^b}$), 1.64 (d, $J = 10.2$ Hz, 6 H, $\mathrm{RuCH^a}H^b$), 0.12 (s, 54 H, $\mathrm{SiCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$, 19 °C): δ 127.51 (s, $\mathrm{CuN}C\mathrm{CH_3}$), 29.70 (s, $\mathrm{RuCH_2}$), 14.64 (s, $\mathrm{CuNC}C\mathrm{H_3}$), 1.21 (s, $\mathrm{SiCH_3}$). Electrochemistry: $E_{1/2}$ of reversible 1e couple at −0.05 V and irreversible oxidations at +0.80 and +1.45 V at 4015 mV/s.

Synthesis of $[Cu(PPh_3)_2][(Ru(N)Me_2)_3S_2]$ (7). $Cu(PPh_3)_2(NCCH_3)_2PF_6$ (0.038 g, 0.046 mmol) was added all at once to a yellow solution of **2** (0.039 g, 0.046 mmol) in 25 mL of CH_2Cl_2, and the mixture was magnetically stirred at room temperature for 1 h. Solvent was removed under vacuum, and the residue was extracted with diethyl ether and filtered through Celite, removing $[PPh_4][PF_6]$. The solvent was removed from the filtrate under vacuum, and the residue was dissolved in CH_2Cl_2. Hexane was added to the yellow solution, and the mixture was cooled to −30 °C. Complex **7** (0.020 g, 0.018 mmol, 39.5%) was collected by filtration as a yellow solid. IR (KBr pellet, cm^{-1}): 3052 (w, υ_{CH}), 2968 (w, υ_{CH}), 2885 (w, υ_{CH}), 2772 (w, υ_{CH}), 1474 (s, $\delta_{C=C}$), 1436 (vs, $\upsilon_{C=C}$), 1186 (s, δ_{CH}), 1072 s (υ_{RuN}), 989 s, 746 (s, δ_{CH}), 685 (vs, δ_{CH}) 526 (s, δ_{CH}), 511 (s, δ_{CH}). ^1H NMR (400 MHz, $CDCl_3$, 19 °C): δ 7.43 (m, 2 H, *p*-PC_6H_5), 7.31 (m, 6 H, *o*-PC_6H_5), 7.19 (m, 6 H, *m*-PC_6H_5), 1.68 (s, 9 H, $RuCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 19 °C) δ 133.43 (d, $J = 3.2$ Hz, *p*-C_6H_5), 130.44 (d, $J = 14.4$ Hz, *m*-PC_6H_5), 129.08 (d, $J = 8.3$ Hz, *o*-PC_6H_5), 116.68 (d, $J = 89.2$ Hz, *ipso*-PC_6H_5), 2.55 (s, $RuCH_3$). Anal. Calcd for $C_{42}H_{48}N_3P_2S_2CuRu_3$: C, 46.38; H, 4.45; N, 3.86; Cu, 5.84. Found: C, 46.15; H, 4.65; N, 4.12; Cu, 5.47.

Conductivity Studies of 4 and 7. A solution of each compound (0.006−0.032 g) in 2.0 mL of CH_2Cl_2 was placed into an electrochemical cell containing a Pt working microelectrode, a Pt-wire auxiliary microelectrode, and a Ag/AgCl aqueous reference microelectrode. The internal resistance of the cell was measured. The conductivities of **4**, **7**, and $Ru(N)(CH_2SiMe_3)_3(NC_5H_6)$ were determined: **4**, 44.4 $\Omega^{-1}\cdot cm^3\cdot mol^{-1}$; **7**, 48.7 $\Omega^{-1}\cdot cm^3\cdot mol^{-1}$; $Ru(N)(CH_2SiMe_3)_3(NC_5H_5)$, 11.2 $\Omega^{-1}\cdot cm^3\cdot mol^{-1}$.

Reaction of 1 with PPh_3. A solution of **1** (0.005 g, 0.007 mmol) in 0.75 mL of $CDCl_3$ was added to a 5-mm NMR tube. An initial ^1H NMR spectrum confirmed the presence of **1**. Excess PPh_3 (0.008 g, 0.030 mmol) was added to the NMR tube. The reaction was followed by ^1H and ^{31}P NMR spectroscopy. After 30 min, no **1** remained in solution. The ^{31}P NMR spectrum showed resonances of approximately equal intensity for $S{=}PPh_3$ (δ 44) and unreacted PPh_3 (δ 4.5) along with several resonances between δ 26 and 18.

Reaction of 2 with PPh_3. A solution of **2** (0.015 g, 0.010 mmol) in 0.75 mL of $CDCl_3$ was added to a 5 mm NMR tube. An initial ^1H NMR spectrum confirmed the presence of **2**. Excess PPh_3 (0.018 g, 0.069 mmol) was added to the NMR tube. The reaction was followed by ^1H and ^{31}P NMR spectroscopy. After 2 h, most of the starting material remained unreacted but small quantities of $S{=}PPh_3$ (δ 44) and of a new osmium phosphine complex (δ 24) were observed in the ^{31}P NMR spectrum. After 24 h, approximately 50% of **2** had been converted to $S{=}PPh_3$ and an osmium phosphine complex.

Reaction of 4 with PPh_3. A solution of **4** (0.010 g, 0.012 mmol) in 0.75 mL of $CDCl_3$ was added to a 5-mm NMR tube. Excess PPh_3 (0.006 g, 0.023 mmol) was added to the NMR tube. The reaction was followed by ^1H and ^{31}P NMR spectroscopy. After 2 h, most of the starting material remained unreacted but a small quantity of $S{=}PPh_3$ (δ 44) and of a new ruthenium phosphine complex (δ 23.8) were observed in the ^{31}P NMR spectrum. After 24 h, the ^{31}P NMR showed an increase in the intensity of the $S{=}PPh_3$ and ruthenium phosphine resonances. Most of **4** had remained unreacted as determined by ^1H NMR, however.

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Supplementary Material Available: For $[N(n\text{-}Bu)_4][\{Os(N)(CH_2SiMe_3)_2\}_3(\mu_3\text{-}S)_2]$, tables of additional crystallographic data, atomic coordinates, thermal parameters, and additional distances and angles (11 pages). Ordering information is given on any current masthead page.

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