Inorg. Chem. **1993**, *32*, 5646–5651

Articles

Osmium(VI) Complexes of Tetrathiotungstate

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Received February 11, 1993[⊗]

The anionic organoosmium complexes $[Y][Os(N)R_2Cl_2]$ ($Y = PPh_4, NBu_4$; $R = CH_3, CH_2SiMe_3$) reacted with $(NH_4)_2WS_4$ or $(NH_4)_2MoS_4$ to give the heterobimetallic complexes $[Y][Os(N)R_2(\mu\text{-}S)_2MS_2]$ ($M = W, Mo$). The reaction of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with an excess of $(NH_4)_2WS_4$ in CH_2Cl_2 at room temperature produced a trimetallic complex in which two organonitridoosmium units are bridged by a tetrathiotungstate group, $(Me_3SiCH_2)_2(N)Os(\mu\text{-}S)_2W(\mu\text{-}S)_2Os(N)(CH_2SiMe_3)_2$. The molecular structures of $[NBu_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]$ and $[(Me_3SiCH_2)_2(N)Os]_2(\mu\text{-}WS_4)$ were determined by X-ray diffraction. Crystals of $[NBu_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]$ are monoclinic in space group $C2/c$ with $a = 39.358(9)$ Å, $b = 11.074(3)$ Å, $c = 18.685(9)$ Å, $\beta = 109.37(3)°$, $Z = 8$, $R = 0.040$, and $R_w = 0.048$. Crystals of $[(Me_3SiCH_2)_2(N)Os]_2(\mu\text{-}WS_4)$ are triclinic in space group $P\bar{1}$ with $a = 10.012(3)$ Å, $b = 11.979(5)$ Å, $c = 15.775(4)$ Å, $\alpha = 105.51(3)°$, $\beta = 97.34(2)°$, $\gamma = 112.03(3)°$, $Z = 2$, $R = 0.026$, and $R_w = 0.030$. The reaction between $[(Me_3SiCH_2)_2(N)Os]_2(\mu\text{-}WS_4)$ and Ph_4PCl gave $[PPh_4]_2[R_2Os(N)Cl]_2(\mu\text{-}WS_4)$.

Introduction

Polymetallic sulfides have attracted the attention of the chemical community because of their applications in catalysis, their solid-state properties, and their relevance to iron–sulfur metalloenzymes.[1] One method for the synthesis of polymetallic sulfides is the reaction between tetrathiometalates and transition metal coordination compounds.

The tetrathiomolybdate and tetrathiotungstate anions, MoS_4^{2-} and WS_4^{2-}, coordinate very well to a variety of transition metals due to the excess electron density on the sulfur atoms and the accessible empty orbitals on the molybdenum and tungsten atoms.[2] The molecular structures of these inorganic coordination compounds usually show the tetrathiometalate moiety chelating to a metal through two sulfur bridges, as in $S_2W(\mu\text{-}S)_2Co(bpy)_2$[3] or $[PPh_4]_2[\{S_2W(\mu\text{-}S)_2\}_2Fe(DMF)_2]$,[4] or bridging two transition metals with all four sulfur atoms, as in $[PPh_4]_2[Cl_2Fe(\mu\text{-}S)_2W(\mu\text{-}S)_2FeCl_2]$.[5] Other bonding modes are known but are less common.

Recently, organometallic tetrathiometalate complexes were prepared. The organometallic fragments are in relatively low oxidation states and contain π-acceptor diene, arene, cyclopentadienyl, or carbonyl ligands.[6–13] The tetrathiometalate moiety seems to be rather unreactive in these complexes, but conversion of the coordinated tetramethylbutadiene ligand in $[(C_4Me_4)NiCl]_2WS_4$ to free tetramethylthiophene has been reported by Rauchfuss.[8]

We have previously prepared organoosmium(VI) complexes of perrhenate,[14] chromate,[15] and tungstate.[16] We recently extended this work to include heterometallic complexes containing tetrathiomolybdate and tetrathiotungstate. Here we report the synthesis, characterization, and reaction chemistry of some of these.

Results

Synthesis of Tetrathiotungstate and Molybdate Complexes. The reaction of *trans*-$[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with 1 equiv of $(NH_4)_2WS_4$ produced the osmium tetrathiometalate complex $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$ (**1**)[17] (Scheme I). The yellow product crystallized from methylene chloride/hexane in 81% yield. The methyl complex $[PPh_4][Os(N)(CH_3)_2WS_4]$ (**2**) was prepared in an analogous manner from $[PPh_4][Os(N)(CH_3)_2Cl_2]$ and the tetrathiotungstate salt.

These complexes were characterized by spectroscopic techniques and elemental analysis. They are thermally stable, stable to air, and soluble in organic solvents. The ^{1}H NMR spectrum of **1** shows two doublets at δ 3.17 and 2.16 for the diastereotopic methylene protons and a singlet at δ –0.02 for equivalent methyl protons of the (trimethylsilyl)methyl ligand. The ^{1}H NMR spectrum of the methylosmium complex, **2**, has a single resonance at δ 2.61 for the equivalent methyl groups. The infrared spectra of both complexes display a strong band near 1105 cm^{-1} and a

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

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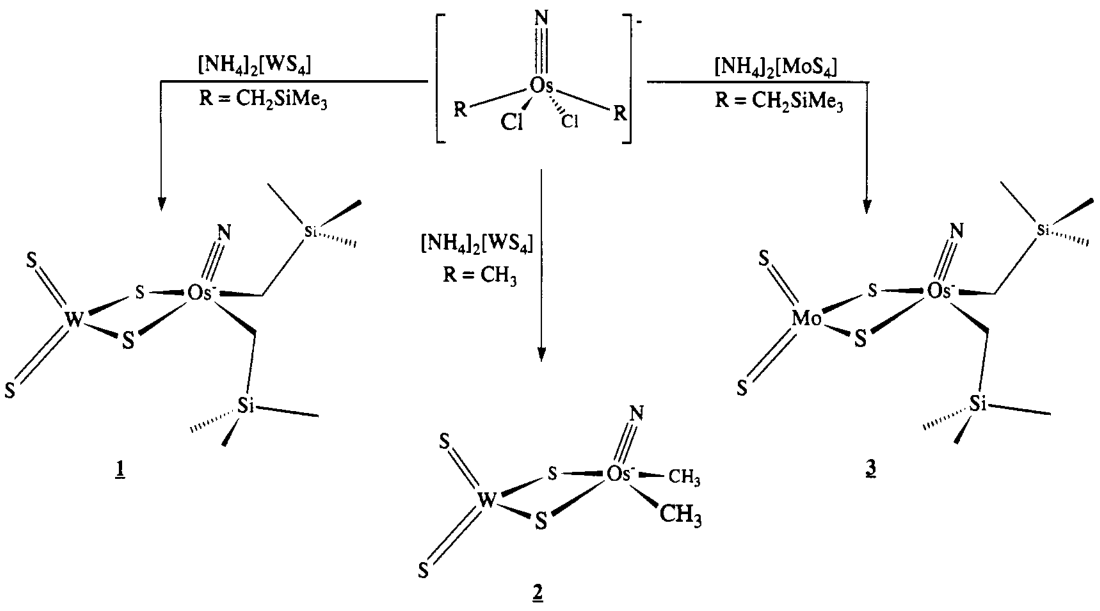
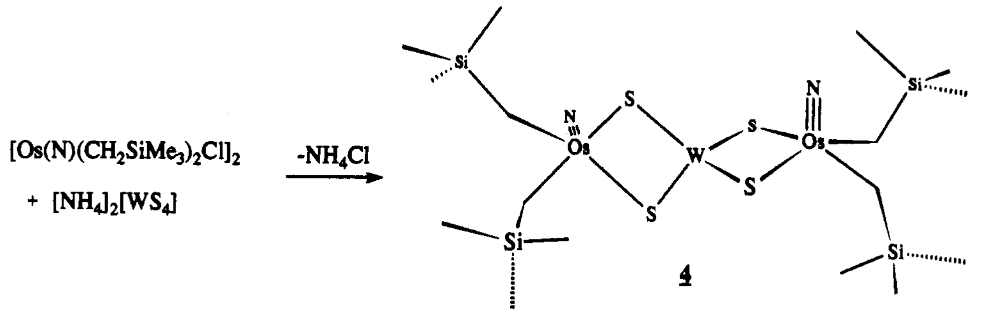
Scheme I



Scheme II



very strong band near 500 cm^{-1} that can be assigned to the osmium–nitrogen and terminal tungsten–sulfido stretching vibrations, respectively. The FAB mass spectrum of **1** exhibits a peak assigned to the tetrabutylammonium cation (m/z = 242) in the positive-ion mode and a peak assigned to $[Os(N)(CH_2SiMe_3)_2WS_4]^-$ (m/z = 692) in the negative-ion mode. The pattern of isotope abundance in the parent anion is identical to the calculated pattern. The UV–visible spectra include an intense absorption at 372 nm for the ligand–metal charge-transfer band of the tetrathiotungstate unit in both complexes. The cyclic voltammogram of **1** shows only irreversible waves: a reduction at −1.15 V and an oxidation at 1.20 V in acetonitrile.

The reaction between $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and finely ground $(NH_4)_2MoS_4$ in acetonitrile produced the osmium–tetrathiomolybdate complex $[NBu^n_4][Os(N)(CH_2SiMe_3)_2MoS_4]$ (**3**). After crystallization of the crude product from methylene chloride/hexane, **3** was obtained in 50% yield as analytically pure brown crystals. The ^1H NMR spectrum of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2MoS_4]$ is very similar to that of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$ with two doublets at δ 3.01 and 2.59 for the diastereotopic methylene protons and a singlet at δ −0.03 for the trimethylsilyl group. The IR spectrum of **3** includes a strong band at 1100 cm^{-1} due to the osmium–nitrido unit and two bands at 517 and 503 cm^{-1} due to molybdenum–sulfur stretching vibrations. The UV–visible spectrum includes a strong band for the tetrathiomolybdate unit at 436 nm, corresponding to ligand-to-metal charge transfer of the tetrathiomolybdate unit.

A minor product in the reaction between $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and $(NH_4)_2WS_4$ was $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}WS_4)$. The trimetallic compound, **4**, was prepared in better yield by treatment of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with an excess quantity of $(NH_4)_2WS_4$ in methylene chloride. The yellow product was formed nearly quantitatively by ^1H NMR, but due to its high solubility in all organic solvents, we could obtain it only in up to 56% yield as analytically pure yellow crystals from cold hexane solutions.

The ^1H NMR spectrum of **4** clearly shows two, inequivalent (trimethylsilyl)methyl groups with well-resolved singlets at 0.06 and 0.10 ppm for the trimethylsilyl moieties and four doublets between 3.70 and 3.17 ppm for the methylene protons. The IR spectrum of **4** displays bands at 1102 and 466 cm^{-1} that can be assigned to osmium–nitride and tungsten–sulfide vibrations, respectively. The FAB-MS showed an intense molecular ion peak at m/z = 1070. The UV–visible spectrum of **4** includes a band at 392 nm for the tetrathiotungstate group. Cyclic voltammetry in CH_2Cl_2 shows a reversible reduction at −0.83 V vs SCE.

Molecular Structure of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$. The molecular structure of **1** was determined by X-ray diffraction. Two sulfur atoms bridge a tetrahedral tungsten atom and a distorted square pyramidal osmium center (Figure 1). Crystallographic parameters are shown in Table III, and selected bond distances and angles are shown in Table I. The osmium atom is above the plane of the four basal ligands. This is commonly observed in five-coordinate nitridoosmium complexes. The nitrogen–osmium–sulfur angles are greater than the nitrogen–osmium–carbon angles. This is probably due to repulsion between lone pairs on the nitride and the bridging sulfides. The osmium–nitrogen distance and the average osmium–carbon distance in $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$ are 1.62(1) and 2.12 Å, respectively. The average terminal W=S distance is 2.13 Å, while the average bridging W—S distance is 2.241 Å. The osmium–tungsten distance of 2.897 Å is shorter than the sum of the covalent radii.

Molecular Structure of $[(Me_3SiCH_2)_2Os(N)]_2(\mu\text{-}WS_4)$. The

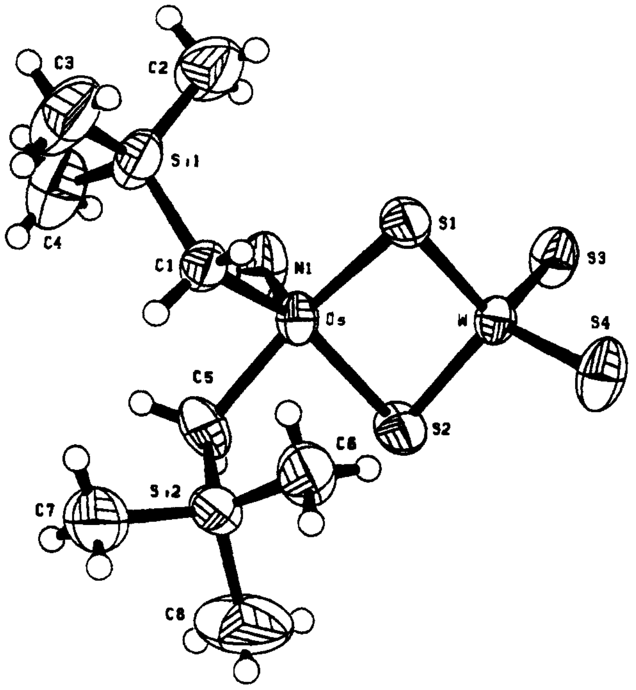


Figure 1. ORTEP diagram of $[Os(N)(CH_2SiMe_3)_2(WS_4)]^-$.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$

Os–W	2.8970(5)	Os–N1	1.62(1)
Os–S1	2.343(3)	Os–C1	2.13(1)
Os–S2	2.349(4)	Os–C5	2.11(1)
W–S1	2.238(3)	W–S3	2.132(4)
W–S2	2.244(3)	W–S4	2.128(4)
Os–S1–W	78.4(1)	N1–Os–C5	102.6(5)
Os–S2–W	78.2(1)	N1–Os–C1	102.3(5)
S1–Os–C1	82.4(3)	S2–Os–C1	148.1(3)
S1–W–S2	103.7(1)	S1–Os–S2	97.3(1)
S1–W–S3	111.4(1)	S1–W–S4	109.6(1)

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[(Me_3SiCH_2)_2Os(N)]_2(\mu\text{-}WS_4)$

Os1–W	2.8372(4)	Os1–N1	1.617(6)
Os2–W	2.8373(4)	Os2–N2	1.631(6)
Os1–S1	2.367(2)	Os1–C1	2.140(6)
Os1–S2	2.357(2)	Os1–C5	2.133(6)
Os2–S3	2.366(2)	Os2–C9	2.130(6)
Os2–S4	2.366(2)	Os2–C13	2.145(7)
W–S1	2.204(2)	W–S3	2.215(2)
W–S2	2.214(2)	W–S4	2.212(2)
Os1–S1–W	76.63(6)	N1–Os1–C5	104.4(3)
Os1–S2–W	76.66(6)	N1–Os1–C1	102.4(3)
Os2–S3–W	76.46(6)	S1–Os1–C1	150.3(2)
Os2–S4–W	76.52(6)	S2–Os1–C5	146.3(2)
S1–W–S2	107.03(7)	S1–Os1–S2	97.49(6)
S1–W–S3	110.24(7)	Os1–W–Os2	166.21(1)
S1–W–S4	112.26(7)	S3–W–S4	106.70(7)

Table III. Crystal Data Collection and Refinement Parameters

	1	4
formula	$OsWS_4Si_2N_2C_{24}H_{58}$	$C_{16}H_{44}Si_4N_2S_4Os_2W$
fw	933.20	1069.38
a, Å	39.358(9)	10.012(3)
b, Å	11.074(3)	11.979(5)
c, Å	18.685(9)	15.775(4)
α, deg		105.51(3)
β, deg	109.37(3)	97.34(2)
γ, deg		112.03(3)
V, $Å^3$	7683(10)	1634(3)
Z	8	2
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
T, °C	26 °C	–75 °C
radiation; λ, Å	Mo Kα;[a] λ(Kα$_1$) = 0.709 30, λ(Kα$_2$) = 0.713 59, λ(Kα) = 0.710 73	
calcd density, (ρ), g cm^{-3}	1.613	2.173
abs coeff (μ), cm^{-1}	66.50	117.53
$R(=\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|)$	0.040	0.026
$R_w\ (=(\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{1/2})$	0.048	0.030

[a] Graphite crystal monochromator.

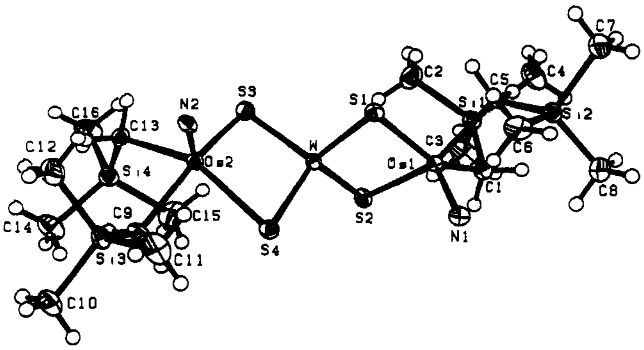


Figure 2. ORTEP diagram of $Os_2(N)_2(CH_2SiMe_3)_4(WS_4)$.

molecular structure was determined by X-ray diffraction on yellow, transparent crystals that were obtained by slowly evaporating a methylene chloride solution of **4** at room temperature. Selected bond distances and angles are presented in Table II, and crystallographic data are given in Table III. The complex contains two osmium centers (Figure 2), in which each osmium is bound to two alkyl groups, the nitride, and two sulfur atoms of the bridging tetrathiotungstate. The geometry around both osmium centers is distorted square pyramidal, with the metals above the plane of the four basal ligands; and that around tungsten metal is distorted tetrahedral with S–W–S angles between 106.70(7) and 112.26(7)°. The tungsten–sulfur bond distances are similar, ranging from 2.204(2) to 2.215(2) Å. The osmium–tungsten distances are shorter than the covalent Os–W distance of 3.140 Å.

Reaction Chemistry of $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ and $[Os(N)(CH_2SiMe_3)_2Cl]_2(\mu\text{-}WS_4)$. The neutral trimetallic complex reacts with chloride to give an addition product. The addition of 2 equiv of tetraphenylphosphonium chloride to a methylene chloride solution of compound **4** gave a gold-colored solution. Analytically pure, yellow crystals of $[PPh_4]_2[R_4Os_2(N)_2Cl_2WS_4]$ (**5**) were collected from methylene chloride/hexane solution in 62% yield. The IR spectrum of **5** included strong bands at 1103 and 528 cm^{-1}, assigned to the osmium–nitride and tungsten–sulfide stretching vibrations. The NMR spectra of **5** show that the alkyl groups are equivalent. The negative-ion FAB-MS showed an intense peak at m/z = 1480 that corresponds to $[PPh_4][R_4Os_2(N)_2Cl_2WS_4]$, and a band at 372 nm in the visible spectrum is associated with the tetrathiotungstate ligand.

The bimetallic complex $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ does not react with tetraphenylphosphonium chloride. It does react with excess aqueous hydrochloric acid to give $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$. Neither **1** nor **4** reacts with carbon monoxide, hydrogen, ethylene, pyridine, or elemental sulfur. There is no reaction between **1** and 1,2-ethanedithiol or benzyl alcohol.

Abstraction of atomic sulfur by thiophilic nucleophiles is a reaction common to sulfido complexes and is of biochemical significance.[18] The active sites of the molybdoproteins xanthine oxidase, xanthine dehydrogenase, and aldehyde oxidase possess a sulfur atom that can be abstracted by cyanide ion to yield the

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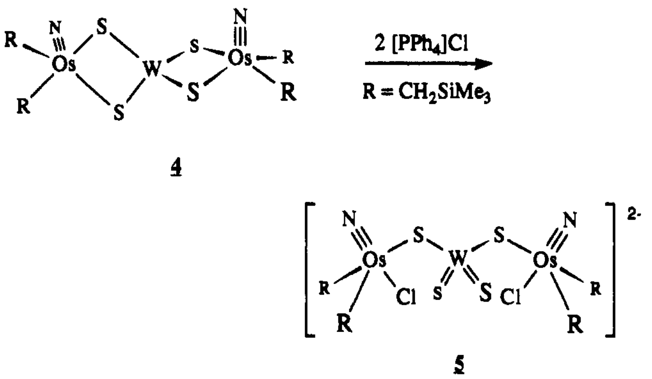
Scheme III



thiocyanate ion and an inactive form of the enzyme.[19] Trimethylphosphine reacted with both **1** and **4** over several hours at room temperature in benzene to give trimethylphosphine sulfide. The phosphine sulfide was characterized by ^1H and ^{31}P NMR, mass spectroscopy, and gas chromatography. We were unable to isolate the organometallic products in either reaction. (Under other reaction conditions, PMe_3 reduced the osmium center in **1**.[17]) Neither $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ nor $[Os(N)(CH_2SiMe_3)_2Cl]_2(\mu\text{-}WS_4)$ reacted with triphenylphosphine.

Discussion

Tetrathiotungstate and tetrathiomolybdate are electron-rich, chelating ligands that readily displace chloride from the osmium center in organometallic nitridoosmium complexes. On the basis of spectroscopic data, these ligands are better donors than chloride but are less electron-donating than alkanethiolate ligands. The osmium–nitrogen stretch, which correlates inversely with electron density of the metal, is 1124 cm^{-1} for $[NBu_4][cis\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$, 1091 cm^{-1} for $[NBu_4][Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$,[20] and 1105 cm^{-1} for $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$. The nitrogen–osmium triple bond stretch can be similarly compared for the neutral osmium complexes: 1128 cm^{-1} for $[Os(N)(CH_2SiMe_3)_2Cl]_2$[21] and 1102 cm^{-1} for $[Os(N)(CH_2SiMe_3)_2]_2(WS_4)$. A comparison of the IR and NMR spectra of $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ and $[NBu_4][Os(N)(CH_2SiMe_3)_2(MoS_4)]$ shows that the tetrathiomolybdate and tetrathiotungstate groups are essentially identical in their ability to donate electron density to the osmium center.

The bond lengths and angles of the $Os(N)(CH_2SiMe_3)_2$ units in **1** and **4** are very similar those of the square pyramidal complex $[NBu_4][Os(N)(CH_2SiMe_3)_4]$.[22] The osmium–nitrogen distance in the tetraalkyl complex (1.631(1) Å) compares with the Os–N distances in **1** (1.62(1) Å) and in **3** (1.617(6) and 1.631(6) Å).

The tungsten center has a slightly distorted tetrahedral geometry in $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ with short terminal W–S distances of 2.132(1) and 2.128(4) Å and longer bridging W–S distances of 2.238(3) and 2.244(3) Å. The terminal W–S distances are shorter than those found in $(NH_4)_2WS_4$ (2.165 Å average)[23] and (p-cymene)$Ru(PPh_3)WS_4$ (2.153 Å average).[8] Comparably short terminal M–S (M = Mo, W) distances have been reported by Coucouvanis and co-workers for the anionic species $[PhS)_2Fe(\mu\text{-}S)MS_2]^{2-}$ (M = Mo, W),[24] by Averill and co-workers for the structures of $[S_2Mo(\mu\text{-}S)_2Fe(SPh)_2]^{2-}$ and $[S_2Mo(\mu\text{-}S)_2FeCl_2]^{2-}$,[25] and by Garner for the structure of $[(PhS)Cu(\mu\text{-}S)_2MoS_2]^{2-}$.[26] The bridging W–S distances in **1** are within the normal range.[8,27] The Os–S distance of 2.346 (average) is 0.06 Å longer than that in $[NBu^n_4][Os(N)(SCH_2CH_2CO_2)_2]$.[28] The tungsten–sulfur distances and angles in **4** are similar to those in the trimetallic complexes $Cp_2Ru_2(MeNC)_2WS_4$ and $WS_4Rh_2(COD)$.[9,10]

The osmium–tungsten distances of 2.8970(5) Å in **1** and 2.8372(4)–2.8373(4) Å in **3** are all shorter than the sum of the covalent radii (3.140 Å) and the Os–S–W angles are acute, indicating some metal–metal interaction.

The lack of reactivity of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2WS_4]$ toward two-electron-donor molecules can be explained by the high oxidation states of both metals and the strong *trans*-labilizing ligands. Carbon monoxide and olefins coordinate most strongly to electron-rich, low-valent metal centers since filled, π-symmetry metal orbitals are required for metal-to-ligand back-bonding. A π-acid ligand would not be expected to bind strongly to osmium(VI) or tungsten(VI) centers. σ-Donor ligands such as pyridine, thiols, and alcohols coordinate very weakly to the open coordination site of osmium in nitridoosmium(VI) alkyl complexes due to the strong *trans* effect of the nitrogen ligand. Similarly, ligands do not add to the tungsten because of the *trans*-labilizing sulfido ligands. Multiple bonding between the tungsten and sulfide ligands also stabilizes the tetrahedral geometry of the tetrathiotungstate moiety.

In the neutral, trimetallic complex $[(Me_3SiCH_2)_2(N)Os]_2(\mu\text{-}WS_4)$, the tetrathiotungstate group bridges the two osmium centers with two sulfur atoms chelating each osmium center. The addition of chloride to osmium displaces one sulfur atom to give a product with an $\eta^1;\eta^1$-tetrathiotungstate bridge, $[(Me_3SiCH_2)_2(N)(Cl)Os{-}S{-}W({=}S)_2{-}S{-}Os(Cl)(N)(CH_2SiMe_3)_2]^{2-}$. An alternative structure of this product with the two chloride ligands on a bridging tetrathiotungstate group, $[(Me_3SiCH_2)_2(N)(Cl)Os(\mu\text{-}S)_2WCl_2(\mu\text{-}S)_2Os(Cl)(N)(CH_2SiMe_3)_2]^{2-}$, can be discounted on the basis of the IR spectrum. The band at 528 cm^{-1} is in a region typical for terminal W═S stretching vibrations and out of the range for the W—S stretch in bridging (W—S—M) tetrathiotungstate complexes. Addition of chloride to the osmium center if favorable because the osmium forms a strong covalent bond with chloride and loses only a weaker interaction from donation of an electron pair of a tungsten sulfide. Tungsten can form stronger π-bonds to the terminal sulfido ligands since these sulfurs are more electron rich than bridging sulfur atoms.

Addition of chloride to the anionic osmium center in **1** is less favorable from an electrostatic standpoint. Also, since there are already two terminal sulfido ligands on tungsten, the displacement of a sulfur from the osmium would not promote an increase in π-bonding of sulfur to tungsten. Chloride only adds to this molecule under acidic conditions when the tetrathiotungstate moiety can be protonated.

Spectroscopic data for compound **5** allow us to propose a structure for the molecule in which two trigonal bipyramidal osmium centers are bridged by an S–W–S unit. The tungsten center would have two terminal sulfides along with the two bridging sulfides. The ^1H NMR shows that all of the alkyl groups are equivalent. Monodentate coordination of the tetrathiotungstate to each osmium center would allow free rotation about the Os–S bonds and equilibrium of the (trimethylsilyl)methyl ligands. IR spectroscopy supports a change in bonding mode for the

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tetrathiotungstate moiety. The increase in the W–S stretching vibration to 528 cm^{-1} for **5** from 466 cm^{-1} for **4** indicates increased multiple-bond character.

Conclusion

Organometallic osmium(VI) complexes of the tetrathiotungstate anion have been prepared, isolated, and characterized. An osmium(VI) complex of tetrathiomolybdate was also synthesized. The tetrathiotungstate group can act as a bidentate ligand for one osmium center. It can also bridge two osmium atoms, in either a monodentate or a bidentate coordination mode. These complexes are thermally stable, and although they are coordinatively unsaturated, they are relatively unreactive toward simple donor molecules.

Experimental Section

All operations were carried out under nitrogen either in a Vacuum Atmospheres drybox or on a Schlenk line. Toluene, diethyl ether, hexane, benzene, and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen. Methylene chloride and acetonitrile were distilled from CaH_2. Triethylamine, pyridine-2-thiol, and 1,2-dithioethane were distilled under nitrogen prior to use. $Mg(CH_2SiMe_3)_2$ was prepared from $Mg(CH_2SiMe_3)Cl$ and dioxane.[29] $[NBu_4][OsNCl_4]$ was prepared according to Griffith.[30] The compounds $[NBu^n_4][Os(N)Cl_2R_2]$,[31] $[Os(N)Cl(CH_2SiMe_3)_2]$,[23] and 1,2-bis(diphenylphosphino)ethane[32] were prepared according to literature methods. Other reagents were purchased and used without further purification. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. NMR spectra were obtained on a Varian XL200, General Electric QE300, or General Electric GN500 FT NMR spectrometer. ^{31}P NMR spectra were recorded on a GN-300 NB instrument operating at 121 MHz. UV–visible spectra were obtained on a Hewlett-Packard Model 8450 photodiode array spectrophotometer. Gas chromatography was performed on a Hewlett-Packard Model 5790 A instrument with an FID detector and nitrogen as the carrier gas by using a 10% Carbowax 20M on Chromosorb W-HP column. The yields were determined by GLC relative to an internal standard. Mass spectra were recorded on a Finnigan MAT CH-5 (EI) or ZAB (FAB). All analyses were performed by the University of Illinois microanalytical service. Electrochemical measurements were made with a BAS 100 electrochemical analyzer. All electrochemistry was done in a Vacuum Atmospheres drybox. Measurements were taken on an approximately 0.01 M solution of the compound of interest using $[NBu_4][BF_4]$ as the supporting electrolyte. A solution of 0.1 M $[NBu_4][BF_4]$ in methylene chloride was prepared from freshly distilled solvent. Potentials are reported vs Ag/AgCl. Molecular structures were determined by the University of Illinois X-ray laboratory.

Preparation of $[NBu^n_4][Os(N)(CH_2SiMe_3)2(WS_4)]$ (1). $(NH_4)_2WS_4$ (0.3 g, 0.86 mmol) was ground to a fine powder and added to a 100-mL round-bottomed flask along with 50 mL of CH_3CN. A solution of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.3 g, 0.43 mmol, in 10 mL of CH_3CN) was added dropwise to the $(NH_4)_2WS_4$ suspension. The mixture was stirred at room temperature under N_2 for 4 days and then filtered. The solvent was removed by vacuum, and the residue was dissolved in a mixture of hexane/methylene chloride. Cooling this solution to –30 °C led to the formation of yellow crytals. These were collected by filtration and dried under vacuum to give pure $[NBu^n_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ (0.38 g, 95%). IR (KBr pellet; cm^{-1}): 2963–2889 (m, ν_{C-H}), 1469 (m, CH_2 and CH_3), 1244 (s, $SiCH_3$), 1105 (s, $\nu_{Os\equiv N}$), 835 (vs, $SiCH_3$), 499 (vs, $\nu_{W=S}$). UV–visible (CH_2Cl_2; λ_{max}, nm (ϵ)): 250 (5260), 278 (4890), 288 sh (4370), 373 (3010). ^1H NMR (CD_2Cl_2, 300 MHz, 295 K): δ 3.17 (d, J = 12 Hz, 2H, $OsC\mathit{H}^aH^b$), 3.14 (m, 8H, NCH_2), 2.76 (d, J = 12 Hz, 2H, $OsCH^a\mathit{H}^b$), 1.62 (m, 8H, $NCH_2C\mathit{H}_2CH_2CH_3$), 1.45 (m, 8H, $NCH_2CH_2C\mathit{H}_2CH_3$), 1.02 (t, J = 8 Hz, 12H, $NCH_2CH_2CH_2C\mathit{H}_3$), –0.02 (s, 18H, $OsCH_2Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$NMR (CD_2Cl_2, 50.3 MHz, 295 K): δ 59.40 (NCH_2), 24.34 ($NCH_2\mathit{C}H_2CH_2CH_3$), 20.17 ($NCH_2CH_2\mathit{C}H_2CH_3$), 13.84 ($NCH_2CH_2CH_2\mathit{C}H_3$), 6.88 ($OsCH_2$), 1.29 ($CH_2Si\mathit{C}H_3$). Anal. Calcd for $OsWN_2Si_2S_4C_{24}H_{58}$: C, 30.89; H, 6.26; N, 3.00. Found: C, 30.90; H, 6.27; N, 2.99. MS (FAB) (*m/z*): $[Os(N)(CH_2SiMe_3)_2(WS_4)]^-$, 692 (100%); $[NBu^n_4]^+$, 242 (100%).

Preparation of $[Ph_4P][Os(N)(CH_3)_2(WS_4)]$ (2). To a solution of $[PPh_4][Os(N)(CH_3)_2Cl_2]$ (0.04 g, 0.062 mmol) in 50 mL of CH_3CN was added finely ground $(NH_4)WS_4$ (0.04 g, 0.124 mmol). The mixture was magnetically stirred for 24 h at room temperature and filtered, and the filtrate was concentrated under vacuum. The residue was dissolved in methylene chloride. Hexane was added, and the mixture was cooled to –30 °C. Yellow crystals were collected by filtration and dried under vacuum (80% yield, 0.044 g). IR (KBr pellet; cm^{-1}): 3049–2886 (m, ν_{C-H}), 1483 (m, CH_3), 1107 (s, $\nu_{Os\equiv N}$), 526 and 501 (vs, $\nu_{W=S}$). ^1H NMR (CD_2Cl_2, 200 MHz, 295 K): δ 7.5–7.9 (m, 10H, PPh_4), 2.61 (s, 3H, $OsCH_3$). $^{13}C\{^1H\}$NMR (CD_2Cl_2, 75 MHz, 295 K): δ 130.5, 130.7, 134.4, 134.5, and 135.7 (PPh_4), –1.23 ($OsCH_3$). Anal. Calcd for $OsWS_4PNC_{26}H_{26}$: C, 35.26; H, 2.96; N, 1.58. Found: C, 35.24; H, 3.03; N, 1.57. MS (FAB) (*m/z*): $[Os(N)(CH_3)_2(WS_4)]^-$, 547 (67%); $[NBu^n_4]^+$, 339 (100%).

Preparation of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2(MoS_4)]$ (3). To a 100-mL round-bottomed flask were added finely ground $(NH_4)_2MoS_4$ (0.040 g, 0.15 mmol) and 40 mL of CH_3CN. A solution of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.030 g, 0.043 mmol, in 5 mL of CH_3CN) was added dropwise to the $(NH_4)_2MoS_4$ suspension with magnetic stirring. The mixture was stirred at room temperature for 4 days and then filtered. The solvent was evaporated under vacuum, and the crude product was crystallized from CH_2Cl_2/hexane at –30 °C. Brown crystals (0.018 g, 50%) were obtained. IR (KBr pellet; cm^{-1}): 2939–2864 (m, ν_{C-H}), 1417 (m, CH_2 and CH_3), 1248 (s, $SiCH_3$), 1100 (s, $\nu_{Os\equiv N}$), 842 (vs, $SiCH_3$), 518 and 503 (vs, $\nu_{Mo=S}$). Visible (CH_2Cl_2; λ_{max}, nm (ϵ)): 436 nm (5880). ^1H NMR (CD_2Cl_2, 300 MHz, 295 K): δ 3.14 (m, 8H, NCH_2), 3.01 (d, 2H, J = 10 Hz, $OsC\mathit{H}^aH^b$), 2.59 (d, 2H, J = 10 Hz, $OsCH^a\mathit{H}^b$), 1.63 (m, 8H, $NCH_2C\mathit{H}_2CH_2CH_3$), 1.45 (m, 8H, $NCH_2CH_2C\mathit{H}_2CH_3$), 1.02 (t, 12H, $NCH_2CH_2CH_2C\mathit{H}_3$), –0.03 (s, 18H, $OsCH_2SiC\mathit{H}_3$). $^{13}C\{^1H\}$NMR (CD_2Cl_2, 75 MHz, 295 K): δ 59.5 (NCH_2), 24.4 ($NCH_2\mathit{C}H_2CH_2CH_3$), 20.2 ($NCH_2CH_2\mathit{C}H_2CH_3$), 13.8 ($NCH_2CH_2CH_2\mathit{C}H_3$), 6.5 ($OsCH_2$), 1.3 ($CH_2Si\mathit{C}H_3$). Anal. Calcd for $OsMoN_2Si_2S_4C_{24}H_{58}$: C, 33.96; H, 6.89; N, 3.30. Found: C, 34.11; H, 6.93; N, 3.35. MS (FAB) (*m/z*): $[Os(N)(CH_2SiMe_3)_2(MoS_4)]^-$, 604 (29%); $[NBu^n_4]^+$, 242 (100%).

Preparation of $[Os(N)(CH_2SiMe_3)_2]_2(\mu\text{-}WS_4)$ (4). To a 100-mL flask containing 15 mL of CH_2Cl_2 and 0.120 g (0.173 mmol) of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ was added $AgBF_4$ (0.070 g, 0.18 mmol). The color changed from orange to green to light brown. After 1 h, the mixture was filtered to remove AgCl and the solution taken to dryness under vacuum. The brown residue was extracted with hexane, and the extract was filtered. The solvent was removed under vacuum and the residue dissolved in 20 mL of CH_2Cl_2. $(NH_4)_2WS_4$ (0.040 g, 0.115 mmol), was added to this solution, and the mixture was stirred overnight. The color changed to yellow. The mixture was filtered and solvent removed from the filtrate under vacuum. The residue was dissolved in 5 mL of hexane and the solution cooled to –30 °C. The product was obtained as a yellow, microcrystalline powder (0.060 g, 64% yield). IR (KBr pellet; cm^{-1}): 2944–2889 (m, ν_{C-H}), 1244 (vs, $SiCH_3$), 1102 (s, $\nu_{Os\equiv N}$), 833 (vs, Si—C), 466 (s, $\nu_{W=S}$). ^1H NMR ($CDCl_3$, 300 MHZ, 18 °C): δ 3.67 (d, J = 10.1 Hz, 1H, $C\mathit{H}^aCH^b$), 3.58 (d, J = 10.1 Hz, 1H, $C\mathit{H}^{a'}CH^{b'}$), 3.24 (d, J = 10.1 Hz, 1H, $CH^aC\mathit{H}^b$), 3.17 (d, J = 10.1 Hz, 1H, $CH^{a'}C\mathit{H}^{b'}$), 0.10 (s, 9H, $Si(CH_3)_3$), 0.063 (s, 9H, $Si(CH_3)_3$). MS (FAB) (*m/z*): 1070. Anal. Calcd for $C_{16}H_{44}Si_4N_2S_4Os_2W$: C, 17.97; H, 4.15; N, 2.62. Found: C, 18.35; H, 4.21; N, 2.68.

Crystallization and Reduction of X-ray Diffraction Data. Yellow crystals of **1** suitable for X-ray crystallographic analysis were grown by vapor diffusion of hexane into a CH_2Cl_2 solution and stored in CH_2Cl_2/hexane under dinitrogen. The data crystal was mounted using epoxy to a thin glass fiber with the (001) scattering planes roughly normal to the spindle axis on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochromator (λ(Mo Kα) = 0.710 73 Å). Data were collected at 26 °C and corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86).[33] The tungsten and osmium atom positions were deduced from a vector map. Subsequent least-squares difference Fourier calculations revealed orientations for the remaining non-hydrogen atoms, including two disordered positions for the cation.

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Unique positions for atoms C20 and C40 were never located; these atoms were constrained to one equivalent site. Anion hydrogen atoms were included as fixed contributors in "idealized" positions, and cation N–C bond lengths were constrained to be equal preceding each cycle of least squares. No other constraints were placed on the proposed model. In the final cycle of least squares, group isotropic thermal parameters were refined for the anion hydrogen atoms and the disordered cation nitrogen and carbon atoms, and anisotropic thermal coefficients were refined for the remaining atoms. Successful convergence was indicated by the maximum shift/error for the final cycle. The relative site occupancy for the major cation orientation converged to 0.612(2). A final analysis of variance between observed and calculated structure factors showed a slight inverse dependence on sin(θ).

Yellow, X-ray-quality crystals of 4 were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature and stored under dinitrogen. The data crystal was mounted using epoxy to a thin glass fiber with the ($2\bar{3}1$) scattering planes roughly normal to the spindle axis on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochromator (λ(Mo Kα) = 0.71073 Å). Data were collected at –75 °C and corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86); correct positions for the Os and W atoms were deduced from an *E* map. Two cycles of least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the remaining non-H atoms. A final analysis of variance between observed and calculated structure factors showed no systematic errors.

Reaction of $[Os(N)(CH_2SiMe_3)_2]_2(\mu\text{-}WS_4)$ with PPh_4Cl. Synthesis of $[Ph_4P]_2\{[Os(N)Cl(CH_2SiMe_3)_2]_2(WS_4)\}$ (5). A solution of PPh_4Cl (0.014 g, 37.4 μmol) in 5 mL of CH_2Cl_2 was added dropwise to a stirred solution of $[Os(N)(CH_2SiMe_3)_2]_2(\mu\text{-}WS_4)$ (0.020 g 18.70 μmol) in 15 mL of CH_2Cl_2. The color changed from light yellow to gold over a 12-h period. The solution was filtered, the filtrate concentrated to one-fourth the original volume and layered with an equal amount of hexane, and the mixture stored at room temperature for 3 days. Yellow, hairlike crystals were formed. These were filtered off, washed with hexane, and dried under vacuum (0.021 g, 61.76%). IR (KBr pellet; cm^{-1}): 3049–2886 (m, ν_{C-H}), 1613, 1580, and 1477 (m, Ph), 1433 (vs, CH_2 and CH_3), 1238 (s, $SiCH_3$), 1103 (s, $\nu_{Os\equiv N}$), 837 (vs, Si—C), 528 (vs, $\nu_{W=S}$). ^{1}H NMR ($CDCl_3$, 300 MHZ, 20 °C): δ 7.93–7.61 ppm (m, 10H, Ph_4P), 3.11 (d, J = 10.1 Hz, 1H, CH^aCH^b), 2.66 (d, J = 10.1 Hz, 1H, CH^aCH^b), –0.04 (s, 9H, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 293 K): δ 23.69. MS (FAB) (*m/z*): 1480, $(PPh_4)\{Os(N)Cl(CH_2SiMe_3)_2\}_2(WS_4)$. Anal. Calcd for $C_{64}H_{84}P_2Cl_2Si_4N_2S_4Os_2W$: C, 42.26; H, 4.65; N, 1.54; Cl, 3.90. Found: C, 43.08; H, 4.50; N, 1.08; Cl, 3.21.

Reactions of 1 and 4. The osmium tetrathiotungstate complexes (0.01 g) were dissolved in 0.75 mL of $CDCl_3$ in a 5-mm NMR tube. Two–five equivalents of either S_8, pyridine, benzyl alcohol, ethanethiol, triphenylphosphine, or cyclohexene was added in each case. ^{1}H NMR spectra were obtained immediately after addition and again after 24 h. In all cases, only starting materials were observed.

The osmium tetrathiotungstate complexes (0.01 g) were dissolved in 0.75 mL of C_6D_6 in a 5-mm NMR tube. One–two equivalents of PMe_3 was added by microliter syringe in each case. ^{1}H and ^{31}P NMR spectra were obtained immediately after addition, after 1 h, and again after 24 h. In each reaction, the NMR spectra showed slow consumption of the starting material and formation of $S{=}PMe_3$.

The osmium tetrathiotungstate complexes (0.01 g) were dissolved in 1.0 mL of $CDCl_3$ in a medium-pressure reaction vessel. In each case, the vessel was charged with either $CH_2{=}CH_2$ (200 psi), H_2 (1000 psi), or CO (1000 psi), and the mixture was stirred for 24 h. The gas was then discharged, and the solution was transferred to an NMR tube under N_2. ^{1}H NMR spectra showed no reaction.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant CHE 88-07707). Spectra were obtained on NMR instruments purchased through grants from the NIH and the NSF (NIH PHS 1532135, NIH 1531957, and NSF CHE 85-14500). P.A.S. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Fellowship.

Supplementary Material Available: For $[NBu_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]$ and $[Os(N)(CH_2SiMe_3)_2]_2(WS_4)$, tables of crystal data collection and refinement parameters, atomic coordinates, thermal parameters, and selected distances and angles (14 pages). Ordering information is given on any current masthead page.