Synthesis and Reactivity of Osmium(VI) Thiolate Complexes, $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ and $[Os(N)(SCH_2Ph)_4]^-$

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Primary, secondary, and tertiary alkanethiolate complexes of osmium(VI) possessing bridging thiolate ligands have been prepared and characterized. The complexes $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ (R = CH_2CH_3, CMe_3, $CHMe_2$, CH_2CHMe_2, CH_2Ph) are synthesized by the reaction of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with alkali metal thiolates. They are air- and water-stable and unreactive toward nucleophiles and electrophiles. Anionic tetrathiolate and tetraalkoxide complexes of osmium(VI) have also been prepared and characterized. Reaction of $[PPh_4][Os(N)Cl_4]$ with $NaSCH_2Ph$ or $LiOCH_2Ph$ in refluxing THF produces $[PPh_4][Os(N)(SCH_2Ph)_4]$ or $[PPh_4][Os(N)(OCH_2Ph)_4]$. Thermolysis of $[PPh_4][Os(N)(SCH_2Ph)_4]$ gives benzyl disulfide, probably via reductive elimination, while the tetraalkoxide complex produces benzaldehyde and benzyl alcohol upon heating in a β-hydrogen elimination reaction.

Introduction

Thiolate ligands are extensively employed in transition metal chemistry and the versatility of sulfur as a ligand in organotransition metal chemistry has been widely established.[1] Alkane- or arenethiolates can bond to one, two, or three metal atoms using one, three, or five electrons, respectively, to interact with the metal centers.[2] Sulfur-containing species are extensively used as catalysts for hydrogenation, hydrodesulfurization, hydrodenitrification, isomerization, and dehydration of fossil fuels.[3] Sulfur-containing amino acids and peptides act as ligands to transition metals in metalloproteins such as isopenicillin N-synthetase, blue copper proteins, cytochromes, iron−sulfur proteins, and several molybdenum-containing enzymes including sulfite oxidase and xanthine oxidase.[4]

Thiolates form very strong bonds to transition metals because of sulfur's polarizability and the availability of electron pairs on the ligand for π-donation.[5] π-donation from sulfur to the metal can stabilize oxidized transition metal centers, so high oxidation state metal-thiolate complexes are known for many of the transition metals in groups 4−8.[6]

We have been interested in the chemistry of high oxidation state organometallic complexes of the iron triad metals possessing sulfur-containing ligands and have prepared several stable ruthenium(VI) and osmium(VI) complexes possessing thiolate ligands. These including $[N(n\text{-}Bu)_4][M(N)\{HNC(O)CH_2CH_2S\}_2]$ (M = Ru, Os),[7] *cis*- and *trans*-$[Os(N)(CH_2SiMe_3)_2(2\text{-}S\text{-}NC_5H_4)]_2$ and *cis*-$[NBu_4][Os(N)(CH_2SiMe_3)_2(\eta^2\text{-}SCH_2CH_2S)]$.[8] We present here the synthesis and reaction chemistry of a series of organoosmium(VI) thiolate complexes. In addition, we have prepared osmium(VI) tetrathiolate and tetraalkoxide complexes and compared their thermal decomposition reactions.

Results

Synthesis of Organoosmium(VI) μ-Thiolate Complexes. The addition of $NaSCH_2CH_3$ to a methylene chloride solution of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ causes the color to change from orange to golden yellow as NaCl precipitates. Removal of the solvent gives an orange oil. Analytically pure $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SCH_2CH_3)]_2$, **1**, can be obtained in approximately 70% yield as a yellow powder from concentrated acetonitrile solutions at −30 °C (Scheme 1).

Complex **1** was characterized by ^1H and ^{13}C NMR spectroscopy, IR, mass spectroscopy, and elemental

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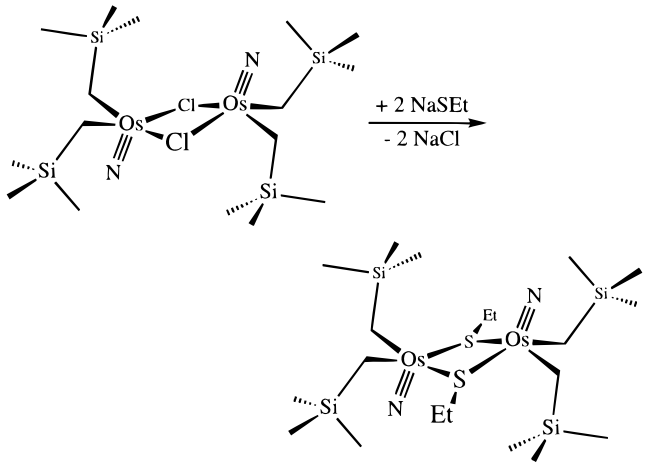
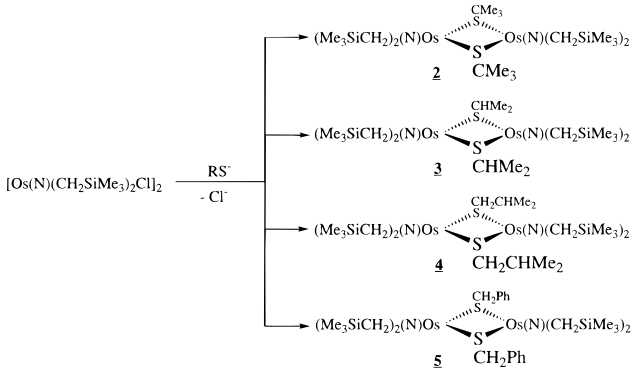
Scheme 1



Scheme 2



analysis. The ^{1}H NMR spectrum shows the presence of two isomers: **1a** (85%) and **1b** (15%). For each isomer, all four (trimethylsilyl)methyl ligands are equivalent and both ethanethiolate ligands are equivalent. The α-protons of the (trimethylsilyl)methyl ligands are diastereotopic. In **1a** the α-protons of the ethanethiolate groups are diastereotopic while in **1b** they are equivalent. The major isomer, **1a**, exhibits two doublets of quartets for the methylene protons as well as a broad triplet for the methyl protons of the ethanethiolate ligand. There are also 2 doublets and a singlet characteristic of the (trimethylsilyl)methyl ligands. For the ethanethiolate protons of **1b** are a quartet and a broad triplet. Two doublets and a singlet for the (trimethylsilyl)methyl protons are clearly visible for **1b**. The ^{13}C{^{1}H} NMR spectrum includes 2 resonances for the ethanethiolate methylene and methyl carbons and 2 resonances for the methylene and methyl carbons of the (trimethylsilyl)methyl ligands of **1a**. There are 4 peaks in the ^{13}C NMR spectrum of **1b** for the corresponding carbons. The IR spectrum of **1** shows bands associated with the (trimethylsilyl)methyl and ethyl thiolate ligands in addition to a band at 1111 cm^{-1} assigned to the Os≡N stretching vibration. This compares well with the osmium−nitrogen stretching vibrations of other neutral nitridoosmium(VI) thiolate complexes possessing similar ligand environments.

The reactions of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with the lithium or sodium salts of 2-methylpropane-2-thiolate, propane-2-thiolate, 2-methylpropanethiolate, and benzyl thiolate, result in the formation of thiolate-bridged bimetallic complexes of the form $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ (R = CMe_3, **2**; $CHMe_2$, **3**; CH_2CHMe_2, **4**; CH_2Ph, **5**) in good yield. Complexes **1**−**5** can also be prepared by treatment of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with the corresponding thiol and a base such as $KOCMe_3$ or NEt_3 (Scheme 2).

The NMR and IR spectra of complexes **2**−**5** are similar to those obtained for **1**. The thiolate α-protons for **3**−**5** fall between 3 and 5 ppm. The ^{13}C{^{1}H} NMR spectra for **3**−**5** include resonances for the α-carbon of the thiolate ligand between 30 and 40 ppm. The osmium−nitrogen stretching vibration in the IR spectra of **2**−**5** fall in a very narrow range, from 1114 to 1117 cm^{-1}, showing that the amount of electron density at osmium is similar for all of these complexes.

Like **1**, each of the μ-thiolate complexes can be prepared as a mixture of isomers. The 2-methylpropane-2-thiolate complex is prepared as a mixture of 2 isomers with the major isomer, **2a**, comprising 87% of the total. In each isomer, the 4 alkyl groups are equivalent with diastereotopic methylene protons and the two 2-methylpropane-2-thiolate ligands are equivalent. Two isomers of **3** are formed when the compound is synthesized from $LiSCHMe_2$ and $[Os(N)(CH_2SiMe_3)_2Cl]_2$ (**3a**, 78%; **3b**, 22%) but 3 isomers are produced when the compound is synthesized using a base and the thiol (**3a**, 61%; **3b**, 13%, **3c**, 26%). Each of the isomers of **3** have equivalent alkyl groups with diastereotopic methylene protons and each have equivalent propane-2-thiolate ligands. In isomer **3c**, the methyl groups on the thiolate ligands are diastereotopic while in **3a** and **3b** the corresponding methyl groups are equivalent. Compound **4** is prepared as a single isomer from reaction of the osmium chloride with $HSCH_2CHMe_2$ and $KOCMe_3$ but is formed as a 1:1 mixture of 2 isomers with $LiSCH_2CHMe_2$. Complex **4a** has equivalent alkyls with diastereotopic methylene protons. The thiolate ligands are also equivalent, but the α protons and β methyl groups on the 2-methylpropanethiolate ligands are diastereotopic. The reaction of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ with $KOCMe_3$ and $HSCH_2Ph$ gives two isomers. Complexes **5a**,**b** are formed in variable ratios depending on reaction conditions. A single isomer, **5b**, is formed in the reaction between $[Os(N)(CH_2SiMe_3)_2Cl]_2$ and $LiSCH_2Ph$. The ^{1}H NMR shows that **5b** has equivalent alkyls and equivalent thiolate ligands with diastereotopic α-protons on each. The α-protons on the alkyl groups and on the benzyl thiolate ligands are multiplets in the ^{1}H NMR, indicating that these groups are not equivalent.

The neutral thiolate complexes are stable toward air and water. They are thermally stable, decomposing near 150 °C in the solid state, while in solution they decompose slowly at 120 °C. They exist as yellow or orange solids or oils and are soluble in a wide variety of organic solvents including methylene chloride, ether, and hexane.

Reactions of Organoosmium(VI) Thiolate Complexes. Complexes **1**−**5** are coordinately unsaturated, 16-electron, dimers. They might be expected to react with donor molecules to form stable monomeric thiolate complexes. The bridging chloride complex $[Os(N)(CH_2SiMe_3)_2Cl]_2$ reacts readily with pyridine, PPh_3, or dppe to form monomeric adducts, $Os(N)(CH_2SiMe_3)_2(L)Cl$ (L = NC_5H_5, PPh_3, dppe).[9] We have observed no reaction between any of the complexes **1**−**5** and any amine or arylphosphine. In particular we have monitored the

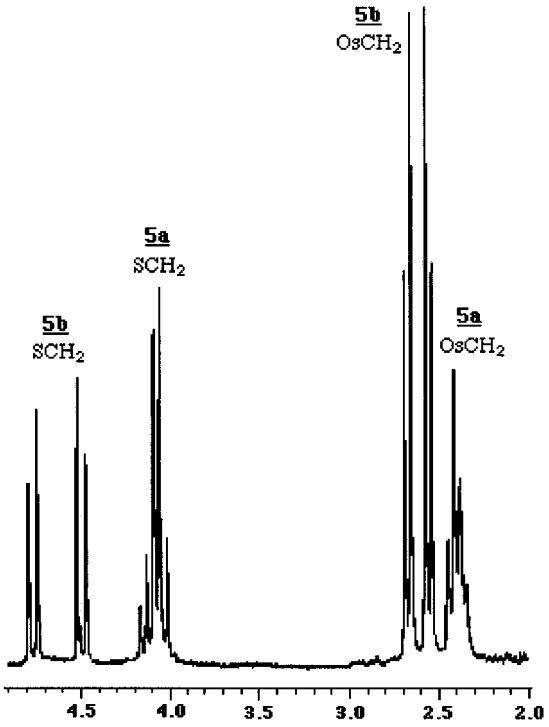


Figure 1. Partial ^{1}H NMR spectrum of $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SCH_2Ph)]_2$.

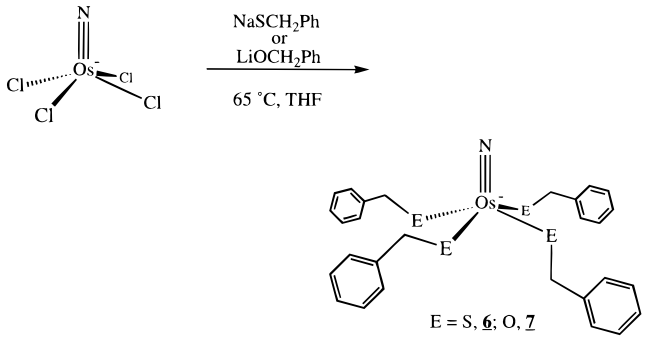
interaction of **5** with pyridine, PPh_3, or TMEDA under conditions where solvent, concentration of donor molecule, and temperature have been varied and have no evidence of reaction prior to the thermal decomposition of **5**.

We have previously shown that nitridoosmium(VI) thiolates and sulfides react with electrophiles at sulfur rather than at the nitride ligand. For example, reaction of the anionic dithioethane complex, $[NBu_4][Os(N)(CH_2SiMe_3)_2(\eta^2\text{-}SC_2H_4S)]$, with (methyl)trifluoromethane sulfonate yields the neutral thiolate−thioether complex, $Os(N)(CH_2SiMe_3)_2(\eta^2\text{-}SC_2H_4SMe)$. However, complex **5** does not react with protic acids or with $Me_3SiOSO_2CF_3$. There is no reaction between **5** and $KOBu^t$, NaH, or $[N(n\text{-}Bu)_4][OH]$.

Heating the osmium thiolate complexes in toluene-d_8 at 115−120 °C results in their slow decomposition. Decomposition of **1** produces Me_4Si, $Me_3SiCH_2CH_2SiMe_3$, and an insoluble osmium species. Heating **5a** in $CDCl_3$ at 115−120 °C led to its complete conversion to **5b**. Continued heating produced small amounts of Me_4Si and $PhCH_2SSCH_2Ph$.

Synthesis of Tetrathiolate and Tetraalkoxide Complexes. Thermal decomposition of metal alkanethiolate complexes could proceed by several pathways analogous to the common decomposition pathways of metal alkyl complexes. Decomposition studies of complexes **1**−**5** are complicated by reactions of the alkyl ligands. In order to study thermolysis of the osmium(VI) thiolate moiety, we prepared a related thiolate complex without alkyl ligands, $[Os(N)(SCH_2Ph)_4]^-$. We also prepared $[Os(N)(OCH_2Ph)_4]^-$ so that decomposition of the thiolate ligand could be compared directly with the corresponding alkoxide ligand.

Scheme 3



Heating a mixture of $NaSCH_2Ph$ and $[PPh_4][Os(N)Cl_4]$ in THF to reflux causes the color of the solution to change from pink to golden-yellow and a white solid to precipitate. The product, $[PPh_4][Os(N)(SCH_2Ph)_4]$, **6**, can be isolated in 55% yield as bright orange crystals. Reaction of $[PPh_4][Os(N)Cl_4]$ with excess $LiOCH_2Ph$, in refluxing THF, leads to formation of the analogous tetraalkoxide complex $[PPh_4][Os(N)(0CH_2Ph)_4]$, **7** (Scheme 3). Both of these compounds are air- and moisture-stable and soluble in organic solvents such as CH_2Cl_2 and THF. Treatment of $[N(n\text{-}Bu)_4][Os(N)(OSiMe_3)_4]$ with an excess quantity of $PhCD_2OH$ gave $[N(n\text{-}Bu)_4][Os(N)(OCD_2Ph)_4]$, **8**.

Complexes **6**−**8** were characterized by IR, NMR spectroscopy, and elemental analysis. The ^{1}H NMR spectrum of **6** shows a sharp singlet at δ 4.24 for the methylene protons of the four equivalent thiolate ligands, while **7** exhibits a singlet at 4.64 for the alkoxide methylene protons. A singlet is also observed in the $^{13}C\{^1H\}$ NMR spectrum of **6** at 31.8 ppm for the benzylic carbons of the thiolate ligands. Complex **7** exhibits a singlet at 65.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The osmium−nitrogen stretching vibration in the IR spectrum of both complexes is obscured by the very strong P−C bending mode of the cation.

Samples of **6** and of **7** were dissolved in toluene-d_8, sealed in NMR tubes under nitrogen, and heated to 70−90 °C. Thermolysis of **6** under these conditions led to the formation of benzyl disulfide, presumably via reductive elimination of the thiolate ligands. There was no thiol, $PhCH_2SH(D)$, produced. However, thermolysis of **7** led to the formation of benzaldehyde and benzyl alcohol in a 1:1 molar ratio as confirmed by ^{1}H NMR and gas chromatographic analysis. No other organic products were detected. Thermolysis of a 1:1 mixture of $[PPh_4][Os(N)(OCH_2Ph)_4]$ and $[N(n\text{-}Bu)_4][Os(N)(OCD_2Ph)_4]$ under the same conditions produced only PhCHO, PhCDO, $PhCH_2OH(D)$, and $PhCD_2OH(D)$. None of the monodeuterated alcohol, PhCHDOH, was produced.

Discussion

The dimeric structures of organoosmium(VI) thiolate complexes **1**−**5** are not surprising given the known tendency for sulfur ligands to bridge two or even three osmium centers. Closely related μ-hydroxo complexes, $[M(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$ (M = Os, Ru), have been prepared, and the structure of the ruthenium complex was determined by X-ray crystallography.[10] These compounds also exist as mixtures of isomers (Figure 2).

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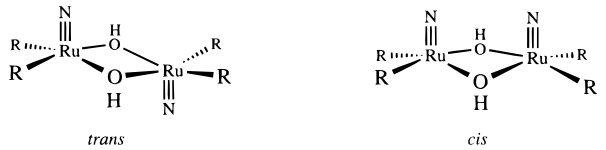

Figure 2. Isomers of $[Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$.

The minor *cis* isomer has nitrido ligands on the same side of the molecule, while the major *trans* isomer has the nitrido ligands on opposite sides of the molecule. The ability of sulfur ligands to bridge osmium(VI) centers has been well established.[8,11,12] The interaction between the osmium atoms and the bridging sulfur is strong. This is demonstrated by our failure to prepare neutral, monomeric organoosmium(VI) thiolate complexes by the reaction of $Os(N)(CH_2SiMe_3)_2(py)Cl$ with 1 equiv of $NaSCH_2Ph$ or by treatment of **5** with excess pyridine.

The ^1H NMR spectra of the isomers of **1**−**5** allow tentative assignments of their structures. The five possible stereoisomers for any of the compounds $[Os(N)R'_2(\mu\text{-}SR)]_2$ are shown in Figure 3. NMR studies have been used to characterize isomers of zirconium μ-thiolate complexes.[13] As in $[Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$, the nitrido ligands can have a *trans* or *cis* orientation with respect to one another. The orientation of the S-alkyls with respect to one another is indicated by *syn* or *anti*. Of these, only the *cis*−*syn* isomers would have equivalent alkyl ligands and equivalent thiolate groups. For R = CH_2CH_3, CH_2CHMe_2, and CH_2Ph the α-protons of the thiolate ligands would be equivalent for the *cis*−*syn* isomers but would be diastereotopic for each of the other isomers. The thiolate ligands would be inequivalent for the *cis*−*anti* isomer. There should be 2 sets of different alkyl groups in the *trans*−*anti*, *trans*−*syn*, and *cis*−*anti* isomers. A concerted inversion of the sulfur atoms of both thiolate ligands would equilibrate the alkyl groups. Inversion of only one thiolate ligand would interconvert *trans*−*anti* with *trans*−*syn* and *cis*−*anti* with the *cis*−*syn* isomers. Similar isomerizations of other bridging thiolate complexes have been proposed to occur through sulfur inversion.[14] Interconversion of *cis* and *trans* forms could only take place through a pathway in which at least one Os−S bond breaks. Studies with various nucleophiles show that such a dissociation does not occur.

With equivalent alkyl groups and diastereotopic ethanethiolate α-protons, **1a** most likely has a *trans*−*anti* structure, and the minor isomer, **1b**, with the equivalent ethanethiolate α-protons is one of the *cis*−*syn* isomers. Isomers **3a**,**b** have equivalent propane-2-thiolate methyl groups and must have *cis*−*syn* structures. For steric reasons, major isomer is probably *cis*−*syn*-2. Isomer **3c** has equivalent alkyl groups and diastereotopic propane-2-thiolate methyl groups and most likely has a *trans*−*anti* structure. Isomer **4a** with equivalent alkyl groups and diastereotopic 2-methylpropanethiolate α-protons and β-methyl groups should have a *trans*−*anti* structure. With its inequivalent alkyl groups and diastereotopic 2-methylpropanethiolate α-protons and β-methyl groups, **4b** should have a *trans*−*syn* structure. The benzyl thiolate complex also probably exists as a mixture of *trans*−*anti* (**5b**) and *trans*−*syn* (**5a**) isomers. The kinetic product would isomerize to the thermodynamically favored product through the inversion of one bridging sulfur.

β-Hydrogen elimination is a common pathway for the decomposition of transition metal alkyl complexes. While nitridoosmium(VI) alkyl complexes are thermally stable for those alkyls that do not have β-hydrogen atoms, the osmium ethyl complex $[N(n\text{-}Bu)_4][Os(N)(CH_2CH_3)_4]$ decomposes at room temperature in solution to give ethene and a mixture of osmium hydrides.[15] β-Hydrogen elimination is also a major route to the decomposition of metal−alkoxide complexes for those alkoxides bearing β-protons.[16] Similar reactions of metal−thiolate complexes are much more rare.[17] Metal thioaldehyde complexes have been prepared by hydride abstraction rather than β-hydrogen elimination.[18] Thiolate complexes have several possible decomposition pathways including S−C bond scission[19] and M−S homolysis[20] or reductive elimination.[21]

While complexes **6** and **7** are similar, thermal decomposition of these complexes follows different pathways. As previously noted, thermolysis of **6** leads to disulfide formation via what appears to be a reductive elimination mechanism (Scheme 4). An alternative to a reductive elimination mechanism is homolysis of the Os−S bond to generate a relatively stable, sulfur-based radical. This radical could cause homolysis of another Os−S bond or dimerize, both of which would result in disulfide formation. In addition, abstraction of a hydrogen atom from the solvent by this radical would lead to formation of benzyl thiol. We do not favor this radical mechanism because no thiol is produced when **6** is heated to decomposition in toluene.

Heating **7** in either toluene-d_8 or acetone-d_6 solutions generates benzaldehyde and benzyl alcohol as the only organic products, and these are always formed in an equimolar ratio. If alkoxy radicals were intermediate in this reaction, some hydrogen abstraction from solvent should increase the percentage of alcohol relative to aldehyde in the product mixture. Thermolysis of a mixture of β-deuterated and nondeuterated alkoxides showed no deuterium scrambling of products indicating that the reaction is intramolecular. The data are consistent with a β-hydrogen elimination mechanism (Scheme 5). The lone pairs of electrons on the other

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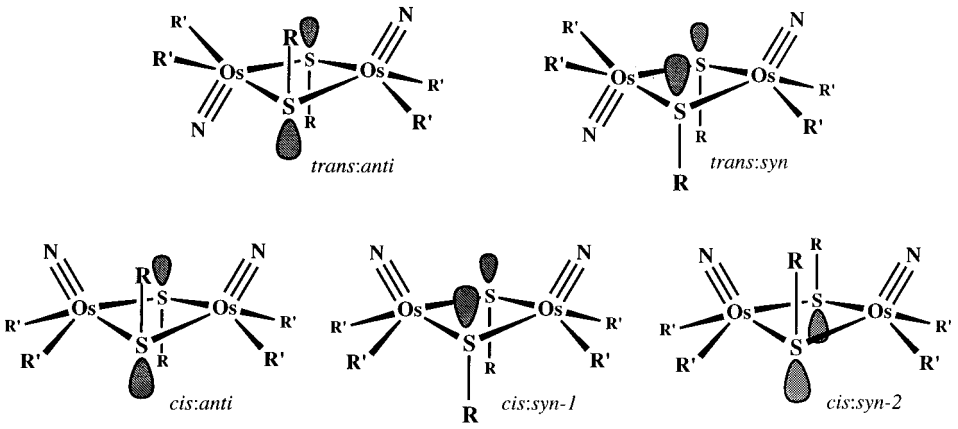
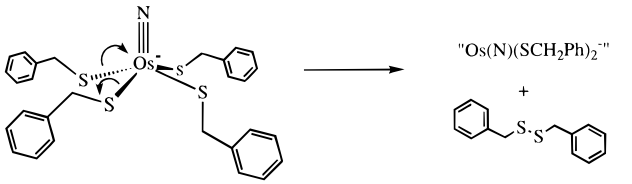
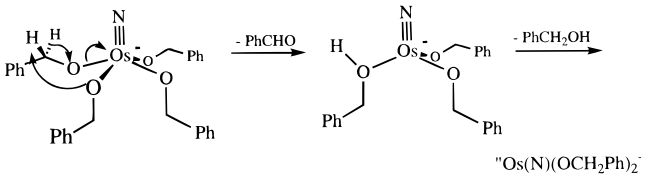


Figure 3. Possible stereoisomers of $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$.

Scheme 4



Scheme 5



alkoxy groups could aid in the β-hydrogen elimination reaction. Base-assisted reductive elimination has been proposed for other transition metal alkoxide complexes.[22]

Conclusion

Primary, secondary, and tertiary alkanethiolate complexes of osmium(VI) possessing bridging thiolate ligands have been prepared and characterized. These neutral complexes are air- and water-stable and unreactive toward nucleophiles and electrophiles. While these are coordinately unsaturated, 16-electron complexes, they are unreactive toward neutral donor ligands.

Anionic tetrathiolate and tetraalkoxide complexes of osmium(VI) have also been prepared. Thermolysis of **6** and **7** leads to distinctly different products. Thermolysis of **6** leads only to benzyl disulfide, probably via a simple reductive elimination process. Complex **7**, however, produces benzaldehyde and benzyl alcohol upon heating in what is the first example of β-hydrogen elimination from an osmium alkoxide complex.

Experimental Section

All reactions were done under N_2 using standard air-sensitive techniques on a Schlenk line or in a Vacuum Atmospheres drybox unless otherwise stated. Anhydrous ether, THF, and hexane were distilled from Na/benzophenone. Methylene chloride and CH_3CN were distilled from CaH_2. Toluene was distilled from Na. Deuterated chloroform was distilled from CaH_2 and stored over 4 Å molecular sieves before use. The compounds $[PPh_4][Os(N)Cl_4]$[23] and $[Os(N)(CH_2SiMe_3)_2Cl]_2$[24] were prepared according to literature methods.

NMR spectra were recorded on one of the following spectrometers: GE QE300, Varian U-400, or GE GN500 FT NMR. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. Electronic spectra were recorded on a Hewlett Packard 8452A diode array UV−visible spectrophotometer. Gas chromatographic experiments were performed on a Hewlett Packard 5790 Series gas chromatograph. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Mass spectra were recorded on a VG 70-VSE by the University of Illinois School of Chemical Sciences Mass Spectrometry Laboratory.

Synthesis of $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SCH_2CH_3)]_2$, 1. $NaSC_2H_5$ (0.008 g, 0.070 mmol) was added to a solution of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ (0.033 g, 0.040 mmol) in 20 mL of CH_2Cl_2 with stirring. The reaction mixture was stirred for 45 min during which time the solution changed from orange to yellow and white solid precipitated. The solution was filtered through Celite, and the solvent was removed from the filtrate in vacuum to give a yellow oil. The oil was dissolved in 1 mL of CH_3CN, and the solution was cooled to 30 °C. A fine, yellow solid (0.026 g, 0.030 mmol, 74%) precipitated. This was collected by filtration and dried under vacuum. Mp: 60−62 °C; 150 °C (dec). IR (KBr pellet, cm^{-1}): 2946 (s, ν_{CH}), 2893 (m, ν_{CH}), 1449 (w, δ_{CH}), 1378 (w, δ_{CH}), 1256 (s, δ_{SiC}), 1245 (vs, δ_{SiC}), 1114 (m, ν_{OsN}), 848 (vs, ν_{SiC}), 833 (vs, ν_{SiC}), 714 (m), 683 (m). ^1H NMR (400 MHz, toluene-d_8, 20 °C, 85% **1a** and 15% **1b** by integration, other integrals are relative for that isomer): δ 3.23 (dq, 2 H, SC*H*^{a}H^b, **1a**), 2.97 (dq, 2 H, SCH^a*H*^{b}, **1a**), 2.92 (q, 4H, SCH_2, **1b**), 2.65 (d, 2 H, OsC*H*^{a}H^b, **1b**), 2.61 (d, 2 H, OsC*H*^{a}H^b, **1a**), 2.52 (d, 2 H, OsCH^a*H*^{b}, **1a**), 2.45 (d, 2 H, OsCH^a*H*^{b}, **1b**), 1.31 (br t, 6 H, $OsSCH_2CH_3$, **1b**), 1.23 (br t, 6 H, $OsSCH_2CH_3$, **1a**), 0.20 (s, 18 H, $SiCH_3$, **1a**), 0.13 (s, 18 H, $SiCH_3$, **1b**). $^{13}C\{^1H\}$ NMR (100.6 MHz, toluene-d_8, 20 °C): δ 25.4 (s, SCH_2, **1a**), 23.6 (s, SCH_2, **1b**), 18.4 (s, $OsCH_2$, **1b**), 17.5 (s, $OsCH_2$, **1a**), 8.51 (s, SCH_2CH_3, **1a**), 7.61 (s, SCH_2CH_3, **1b**), 1.73 (s, $SiCH_3$, **1a**), 1.55 (s, $SiCH_3$, **1b**). Anal. Calcd for $C_{10}H_{27}NOsSSi_2$: C, 27.31; H, 6.19; N, 3.19. Found: C, 27.57; H, 6.33; N, 3.26.

Synthesis of $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SCMe_3)]_2$, 2. $LiSCMe_3$ (0.014 g, 0.15 mmol) was added to a solution of $[Os(N)(CH_2SiMe_3)_2Cl]_2$ (0.058 g, 0.07 mmol) in 30 mL of CH_2Cl_2, and the mixture was stirred overnight. The reaction mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuum to give a yellow-brown oil. This oil was

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extracted with hexane and filtered through Celite. The hexane was removed from the filtrate in vacuum and the resulting yellow-brown oil was redissolved in a few milliliters of ether. Bright orange crystals were obtained by slow evaporation of the ether. IR (KBr pellet, cm^{-1}): 2946 (m, ν_{CH}), 2893 (m, ν_{CH}), 1457 (w, δ_{CH}), 1364 (w, δ_{CH}), 1256 (m, δ_{SiC}), 1245 (s, δ_{SiC}), 1142 (m), 1114 (m, ν_{OsN}), 850 (vs, ν_{SiC}), 831 (vs, ν_{SiC}), 720 (m), 681 (m). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, 87% **2a** and 13% **2b** by integration, other integrals are relative for that isomer): δ 2.98 (d, 2 H, J = 10.1 Hz, OsC*H*^{a}H^b, **2b**), 2.87 (d, 2 H, J = 10.5 Hz, OsC*H*^{a}H^b, **2a**), 2.63 (d, 2 H, J = 10.0 Hz, OsCH^a*H*^{b}, **2b**), 2.27 (d, 2 H, J = 10.6 Hz, OsCH^a*H*^{b}, **2a**), 1.19 (s, 9 H, CCH_3, **2b**), 1.68 (s, 9 H, CCH_3, **2a**), 0.11 (s, 18 H, $SiCH_3$, **2a**), 0.01 (s, 18 H, $SiCH_3$, **2b**). Anal. Calcd for $C_{12}H_{31}NOsSSi_2$: C, 30.81; H, 6.68; N, 2.99. Found: C, 30.80; H, 6.84; N, 2.98.

Synthesis of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-SCHMe$_2$)]$_2$, 3. LiSCHMe$_2$ (0.010 g, 0.12 mmol) was added to a solution of [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ (0.044 g, 0.053 mmol) in 15 mL of CH_2Cl_2, and the mixture was stirred overnight. The reaction mixture was filtered through Celite, and the solvent was removed in vacuum from the filtrate to yield a yellow-orange oil. The oil was extracted with hexane and filtered through Celite. The solvent was removed from the filtrate in vacuum to give 0.042 g (0.046 mmol, 87%) of **3** as a yellow-orange oil. IR (KBr pellet, cm^{-1}): 2946 (s, ν_{CH}), 2892 (s, ν_{CH}), 1451 (m, δ_{CH}), 1365 (m, δ_{CH}), 1256 (s, δ_{SiC}), 1243 (vs, δ_{SiC}), 1152 m, 1117 (s, ν_{OsN}), 1049 m, 851 (vs, ν_{SiC}), 831 (vs, ν_{SiC}), 715 (s), 682 (s). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, 78% **3a** and 22% **3b** by integration, integrals are relative for each isomer): δ 4.14 (septet, J = 6.8 Hz, 2H, SCH, **3a**), 3.81 (septet, J = 7 Hz, 2H, SCH, **3b**), 1.71 (d, J = 6.8 Hz, 12H, SCHC*H*$_3$, **3a**), 1.54 (d, J = 7 Hz, 12 H, SCHC*H*$_3$, **3b**), 0.09 (s, 36 H, $SiCH_3$, **3b**), 0.02 (s, 36 H, $SiCH_3$, **3a**). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C): δ 39.4 (s, SCH, **3a**), 38.8 (s, SCH, **3b**), 26.7 (s, $OsCH_2$, **3b**), 26.7 (s, $OsCH_2$, **3a**), 9.04 (s, SCH*C*H$_3$, **3b**), 7.45 (s, SCH*C*H$_3$, **3a**), 1.46 (s, $SiCH_3$, **3b**), 1.41 (s, $SiCH_3$, **3a**). Mass spectrum (EI, 70 eV, m/z): 910 (M^+).

The addition of an equimolar mixture of $HSCHMe_2$ and $KOCMe_3$ to the [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ solution as above led to the formation of an orange oil containing 3 isomers of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-SCHMe$_2$)]$_2$. The ratio of isomers was determined by integration of the ^{1}H NMR spectrum: 61% **3a**, 13% **3b**, and 26% **3c**. Homonuclear decoupling experiments confirmed the proton assignments for the thiolate groups in each isomer. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, integrals are relative for each isomer): δ 4.14 (septet, J = 6.8 Hz, 2H, SCH, **3a**), 3.81 (septet, J = 7 Hz, 2H, SCH, **3b**), 3.65 (br septet, 2 H, J = 6 Hz, SCH, **3c**), 1.71 (d, J = 6.8 Hz, 12H, SCHC*H*$_3$, **3a**), 1.54 (d, J = 6.6 Hz, 12 H, SCHC*H*$_3$, **3b**), 1.35 (d, J = 7 Hz, 6H, SCH*Me*^{a}, **3c**), 1.27 (d, J = 7 Hz, 6H, SCH*Me*^{b}, **3c**), 0.09 (s, 36 H, $SiCH_3$, **3b**), 0.02 (s, 36 H, $SiCH_3$, **3a**), −0.04 (s, 36H, $SiMe_3$, **3c**).

Synthesis of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-SCH$_2$CHMe$_2$)]$_2$, 4. $LiSCH_2CHMe_2$ (0.012 g, 0.12 mmol) was added to the stirring orange solution of [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ (0.041 g, 0.05 mmol) in 15 mL of CH_2Cl_2, and the reaction was stirred overnight. The yellow solution was filtered through Celite and the solvent removed in vacuum from the filtrate. The resulting yellow-orange oil was extracted with hexane and filtered. The solvent was removed from the filtrate in vacuum to give 0.022 g (0.023 mmol, 47%) of **4a** as a yellow-orange oil. The addition of an equimolar mixture of $HSCH_2CHMe_2$ and $KOCMe_3$ to the [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ solution as above also led to the formation of an orange oil containing only **4a**. IR (KBr pellet, cm^{-1}): 2952 (s, ν_{CH}), 2895 (m, ν_{CH}), 1464 (m, δ_{CH}), 1367 (m, δ_{CH}), 1258 (s, δ_{SiC}), 1245 (vs, δ_{SiC}), 1115 (s, ν_{OsN}), 1109 m, 850 (vs, ν_{SiC}), 831 (vs, ν_{SiC}), 715 (m), 682 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 3.33 (dd, J_{am} = 13.3 Hz, J_{ax} = 6.7 Hz, 2 H, SC*H*^{a}H^b), 3.07 (dd, J_{am} = 13.3 Hz, J_{mx} = 7.9 Hz, 2 H, SCH^a*H*^{b}), 2.57 (d, J = 10.3 Hz, 4 H, OsC*H*^{a}H^b), 2.45 (d, J = 10.5 Hz, 4 H, OsCH^a*H*^{b}), 2.14 (m, 2 H, SCH$_2$C*H*Me$_2$), 1.19 (d, J = 4 Hz, 6 H, SCH$_2$CHC*H*^{a}$_3$CH^b$_3$), 1.15 (d, J = 4 Hz, 6 H, SCH$_2$-CHCH^a$_3$C*H*^{b}$_3$), 0.07 (s, 36 H, $SiCH_3$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 20 °C): δ 39.01 (s, SCH$_2$*C*H), 31.24 (s, SCH_2), 21.85 (s, $OsCH_2$), 7.89 (s, SCH$_2$CH*Me*$_2$), 1.58 (s, $SiCH_3$). Mass spectrum (EI, 70 eV, m/z): 938 (M^+).

A solution of $KOCMe_3$ (0.011 g, 0.098 mmol) and $HSCH_2$-$CHMe_2$ (10 μL, 0.092 mmol) in 10 mL of hexane was added to a solution of [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ (0.018 g, 0.021 mmol) in 5 mL of hexane. The mixture was stirred for 12 h and filtered, and the solvent was removed under vacuum. A yellow oil consisting of a 1:1 mixture of 2 isomers of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-SCH$_2$CHMe$_2$)]$_2$ was produced. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, integrals are relative for each isomer): δ 3.31 (dd, J_{am} = 13.3 Hz, J_{ax} = 6.7 Hz, 2 H, SC*H*^{a}H^b, **4a**), 3.05 (dd, J_{am} = 13.3 Hz, J_{mx} = 7.9 Hz, 2 H, SCH^a*H*^{b}, **4a**), 2.79 (dd, J_{am} = 12.5 Hz, J_{ax} = 6 Hz, 2 H, SC*H*^{a}H^b, **4b**), 2.70 (dd, J_{am} = 12.5 Hz, J_{mx} = 6 Hz, 2 H, SCH^a*H*^{b}, **4b**), 2.55 (d, J = 10.3 Hz, 4 H, OsC*H*^{a}H^b, **4a**), 2.43 (d, J = 10.5 Hz, 4 H, OsCH^a*H*^{b}, **4a**), 2.31 (m, 8 H, $OsCH_2$, **4b**), 2.2 (m, 2 H + 2 H, SCH$_2$C*H*Me$_2$, **4a** and **4b**), 1.15 (d, J = 4 Hz, 6 H, SCH$_2$CHC*H*^{a}$_3$CH^b$_3$, **4a**), 1.13 (d, J = 4 Hz, 6 H, SCH$_2$CHCH^a$_3$C*H*^{b}$_3$, **4a**), 0.99 (d, J = 4.9 Hz, 6 H, SCH$_2$-CHC*H*^{a}$_3$CH^b$_3$, **4b**), 1.13 (d, J = 4.9 Hz, 6 H, SCH$_2$CHCH^a$_3$C*H*^{b}$_3$, **4b**), 0.07 (s, 36 H, $SiCH_3$, **4a**), −0.04 (s, 36 H, $SiCH_3$, **4b**).

Synthesis of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-SCH$_2$Ph)]$_2$, 5. $NaSCH_2Ph$ (0.008 g, 0.055 mmol) was added to the stirring orange solution of [Os(N)(CH$_2$SiMe$_3$)$_2$Cl]$_2$ (0.019 g, 0.023 mmol) in 10 mL of THF. The reaction mixture was stirred overnight (16 h). The solution changed from orange to an orange-gold color over the course of the reaction. The solution was filtered through Celite and the solvent removed from the filtrate under vacuum to give a golden oil that was dried in vacuum. The oil was extracted with hexane, and this extract was filtered through Celite. The solvent was removed from the golden filtrate under vacuum to give 0.022 g (0.022 mmol, 95%) of **5a** as a golden oil. Yellow crystals can be obtained by slow evaporation from pentane (mp = 150 °C, dec). Substituting a mixture of $KOCMe_3$ and $HSCH_2Ph$ for the $NaSCH_2Ph$ in the reaction above leads to the production of an orange oil containing 2 isomers in variable ratios. The 2 isomers can be separated by fractional crystallization from pentane. IR (KBr pellet, cm^{-1}): 2946 (s, ν_{CH}), 2892 (m, ν_{CH}), 1257 (s, δ_{SiC}), 1244 (vs, δ_{SiC}), 1129 w, 1114 (m, ν_{OsN}), 1029 m, 969 m, 848 (vs, ν_{SiC}), 833 (vs, ν_{SiC}), 750 (m), 696 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, integrals are relative for each isomer): δ 7.5−7.0 (m, $SCH_2C_6H_5$), 4.75 (d, J = 14.2 Hz, 2 H, SC*H*^{a}H^b, **5b**), 4.48 (d, J = 14.2 Hz, 2 H, SCH^a*H*^{b}, **5b**), 4.10 (m, 4 H, SCH_2, **5a**), 2.64 (d, J = 10.3 Hz, 4 H, OsC*H*^{a}H^b, **5b**), 2.53 (d, J = 10.5 Hz, 4 H, OsCH^a*H*^{b}, **5b**), 2.36 (m, 8 H, $OsCH_2$, **5a**), 0.03 (s, $SiCH_3$, **5a**), - 0.01 (s, $SiCH_3$, **5b**). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 22 °C): δ 144.4 (s, $SCH_2C_6H_5$, **5a**), 137.5 (s, $SCH_2C_6H_5$, **5b**), 128.9 (br s, $SCH_2C_6H_5$, **5b**), 128.9 (s, $SCH_2C_6H_5$, **5a**), 128.7 (s, $SCH_2C_6H_5$, **5a**), 128.0 (s, $SCH_2C_6H_5$, **5b**), 126.1 (s, $SCH_2C_6H_5$, **5a**), 36.4 (s, SCH_2, **5b**), 31.6 (s, SCH_2, **5a**), 13.8 (s, $OsCH_2$, **5b**), 12.5 (s, $OsCH_2$, **5a**), 1.60 (s, $SiCH_3$, **5a**), 1.26 (s, $SiCH_3$, **5b**). Mass spectrum (EI, 70 eV, m/z): 1006 (M^+). λ_{max} = 236 nm.

Synthesis of [PPh$_4$][Os(N)(SCH$_2$Ph)$_4$], 6. [PPh_4][Os(N)-Cl_4] (0.10 g, 0.15 mmol) was suspended in 25 mL of thf. Excess $NaSCH_2Ph$ (0.098 g, 0.67 mmol) was added to the solution, the flask was equipped with a water-cooled condenser, and the solution was heated to reflux overnight (15 h). Over the course of the reaction the solution turned deep yellow. Heating was discontinued, and the reaction was cooled to room temperature. The solution was filtered through Celite and the solvent removed in vacuum from the filtrate to yield a yellow-gold oil. Bright orange crystals (0.086 g, 0.083 mmol, 55%) were obtained from CH_2Cl_2/hexane. IR (KBr pellet, cm^{-1}): 3054 (w, phenyl ν_{CH}), 3020 (w, phenyl ν_{CH}), 2912 (w, ν_{CH}), 1491 (s), 1436 (s , δ_{CH}), 1106 (vs, δ_{PC}), 1068 (s, phenyl δ_{CH}), 1027 (m, phenyl δ_{CH}), 996 (m, phenyl δ_{CH}), 768 (m), 723 (s), 700 (s), 689 (vs), 526 (vs). ^{1}H NMR (400 MHz, $CDCl_3$, 19 °C): δ 7.75 (m, 4 H, p-PC_6H_5), 7.61 (m, 8 H, o- or m-PC_6H_5), 7.38 (m, 8 H, o- or m-PC_6H_5), 7.26 (m, 8 H, $SCH_2C_6H_5$), 7.06 (m, 8 H, $SCH_2C_6H_5$), 6.98 (m, 4 H, $SCH_2C_6H_5$), 4.24 (s, 8 H, SCH_2). ^{13}C{^{1}H} NMR

(100.6 MHz, $CDCl_3$, 19 °C): δ 144.2 (s, *ipso*-$SCH_2C_6H_5$), 135.6 (d, $J_{PC} = 3.1$ Hz, *p*-PC_6H_5), 134.3 (d, $J_{PC} = 10.7$ Hz, *m*-PC_6H_5), 130.7 (d, $J_{PC} = 13.0$ Hz, *o*-PC_6H_5), 129.4 (s, *o*- or *m*-$SCH_2C_6H_5$), 127.7 (s, *o*- or *m*-$SCH_2C_6H_5$), 125.4 (s, *p*-$SCH_2C_6H_5$), 117.2 (d, $J_{PC} = 90.0$ Hz, *ipso*-PC_6H_5), 31.8 (s, SCH_2). Anal. Calcd for $C_{52}H_{48}NOsPS_4$: C, 60.27; H, 4.67; N, 1.35. Found: C, 59.02; H, 4.63; N, 1.33.

Synthesis of $[PPh_4][Os(N)(OCH_2Ph)_4]$, 7. $[PPh_4][Os(N)Cl_4]$ (0.040 g, 0.058 mmol) was suspended in 20 mL of THF. Excess $LiOCH_2Ph$ (0.033 g, 0.29 mmol) was added, the flask was fitted with a condenser, and the reaction was heated to reflux overnight (11 h). The color of the solution changed from the initial pale red color to a golden brown color. The solution was filtered through Celite, and the solvent was removed in vacuum to give a purple-brown oil. IR (KBr pellet, cm^{-1}): 3054 (w, phenyl ν_{CH}), 3023 (w, phenyl ν_{CH}), 2846 (w, ν_{CH}), 1450 (m), 1438 (vs, δ_{CH}), 1107 (vs, δ_{PC}), 1044 (m, phenyl δ_{CH}), 1022 (m, phenyl δ_{CH}), 995 (m, phenyl δ_{CH}), 725 (vs), 689 (vs), 527 (vs). ^1H NMR (400 MHz, $CDCl_3$, 19 °C): δ 8.0−6.9 (m, PC_6H_5, $OCH_2C_6H_5$), 4.64 (s, OCH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 19 °C): δ 145.9 (s, *ipso*-$SCH_2C_6H_5$), 135.7 (d, $J_{PC} = 2.3$ Hz, *p*-PC_6H_5), 134.2 (d, $J_{PC} = 10.7$ Hz, *m*-PC_6H_5), 130.7 (d, $J_{PC} = 13.0$ Hz, *o*-PC_6H_5), 127.4 (s, *o*- or *m*-$SCH_2C_6H_5$), 127.3 (s, *o*- or *m*-$SCH_2C_6H_5$), 125.2 (s, *p*-$SCH_2C_6H_5$), 117.2 (d, $J_{PC} = 90.0$ Hz, *ipso*-PC_6H_5), 65.0 (s, SCH_2).

Synthesis of $[N(n\text{-}Bu)_4][Os(N)(OCD_2Ph)_4]$, 8. Excess $PhCD_2OH$ (0.5 g, 4.5 mmol) was added to a solution of $[N(n\text{-}Bu)_4][Os(N)(OSiMe_3)_4]$ (0.050 g, 0.062 mmol) in 20 mL of thf. After the solution was stirred for 1 h, the solvent and excess $PhCD_2OH$ were removed under vacuum. The resulting orange oil was dissolved in CH_2Cl_2. Toluene and pentane were added, and the solution was cooled. Orange crystals of **8** were formed (0.047 g, 0.053 mmol, 86%). Anal. Calcd for $C_{44}H_{56}D_8N_2O_4Os$: C, 59.83; H (D), 8.22; N, 3.17. Found: C, 59.93; H (D), 7.54; N, 3.20.

Thermolysis of 1. A sample of **1** (0.005 g, 0.006 mmol) in 0.75 mL of toluene-d_8 was heated at 115−120 °C in a sealed NMR tube. The ^1H NMR spectrum of this sample after 62.5 h of heating showed additional peaks between 0.0 and 0.2 ppm, but otherwise the spectrum was largely unchanged. After 6 days of heating, none of the starting material was present by ^1H NMR spectroscopy. Signals due to $Me_3SiCH_2CH_2SiMe_3$ and Me_4Si were present.

Thermolysis of 5. A 0.005 g sample of **5a** was sealed in a 5 mm NMR tube along with 0.75 mL of $CDCl_3$. The solution was heated to 115−120 °C. After 2 h, peaks for **5b** were visible. After 20 h, the original isomer (**5a**) had been completely converted to **5b**. Small amounts of $PhCH_2SSCH_2Ph$, δ 3.58, and $SiMe_4$, δ 0.0, were also present.

Thermolysis of 6. A 0.005 g sample of **6** was dissolved in 0.75 mL of toluene-d_8 and sealed in a 5 mm NMR tube. The solution was heated to 70−90 °C. The ^1H NMR spectrum of this sample after 9 days showed signals due to benzyl disulfide.

Thermolysis of 7. A 0.005 g sample of **7** was dissolved in 0.75 mL of toluene-d_8 and sealed in a 5 mm NMR tube. The solution was heated to 70−90 °C. The ^1H NMR spectrum of this sample after 12 days showed signals due to benzyl alcohol and benzaldehyde. Gas chromatographic analysis of the solution confirmed the presence of benzaldehyde and benzyl alcohol in a 1:1 molar ratio.

Thermolysis of a Mixture of 7 and 8. A solution of 0.055 g of **7** and 0.044 g of **8** in 0.75 mL of acetone-d_6 was sealed in a 5 mm NMR tube. The solution was heated to 97 °C for 6 days. The ^1H NMR spectrum of this sample showed signals due to $PhCH_2OH$ and PhCHO. There was no PhCHDOH observed.

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