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Communications

Synthesis and Reactivity of $[PPh_4][Ru(N)Me_3(SSiMe_3)]$, a Ruthenium(VI) Trimethylsilylanethiolate Complex

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Summary: The anionic organoruthenium complex $[PPh_4][Ru(N)Me_3Br]$ reacts with $NaSSiMe_3$ to give the trimethylsilylanethiolate complex $[PPh_4][Ru(N)Me_3SSiMe_3]$, **1**. Reactions of **1** with CsF or with PPh_4Cl in nitromethane or acetonitrile produce $[PPh_4][Ru(N)Me_3(SH)]$, **2**. The molecular structure of **2** was determined by X-ray diffraction. Complex **1** reacts with $[Os(N)(CH_2SiMe_3)_2(\mu-Cl)]_2$ to form a heterobimetallic complex, $[PPh_4][Me_3(N)Ru(\mu-S)Os(N)(CH_2SiMe_3)_2(NCCH_3)]$, **3**.

Sulfido complexes of transition metals are important as industrial catalysts and as the active site in certain metalloenzymes.¹ While organometallic terminal sulfido complexes are known, the propensity of sulfur to bridge metal centers leads to the vast number of multi-metal sulfido complexes.^{2,3} Due to the ease in which the Si-S bond can be cleaved by halides or oxygen, trialkyl- or trialkoxysilylanethiolate complexes may be viewed as protected metal sulfides. While transition metal trialkylsiloxy complexes are well-known, rela-

tively little has been reported about transition metal trialkylsilylanethiolate complexes.⁴ Most of the work in this area has focused on the synthesis and structure of the trialkylsilylanethiolate complexes, and little is known of their reaction chemistry.⁵ We have prepared and fully characterized a ruthenium(VI) trimethylsilylanethiolate complex and have explored its reactivity.

A variety of sulfur-containing ligands substitute readily for halide ligands in Ru(VI) and Os(VI) complexes. Nitridoalkylosmium(VI) and ruthenium(VI) complexes of tetrathiotungstate, thiolates, and S^{2-} have been prepared by this route.^{6,7} The reaction of $[PPh_4][Ru(N)Me_3Br]$ with 1.3 equiv of $NaSSiMe_3$ in CH_2Cl_2 at room temperature produces $[PPh_4][Ru(N)Me_3SSiMe_3]$, **1** (Scheme 1). The yellow product crystallizes from CH_2Cl_2 /ether/hexane in 61% yield.⁸

As expected due to the difference between the Si-X

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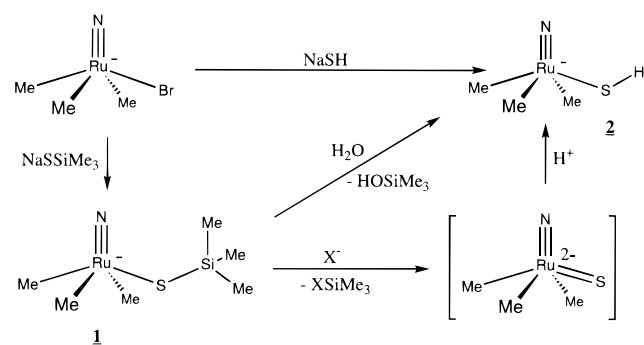
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Scheme 1



and Si–S bond strengths, **1** reacts readily with halide sources such as CsF or PPh_4Cl in nitromethane or acetonitrile to generate Me_3SiF or Me_3SiCl , respectively. The formation of Me_3SiCl in this reaction was followed by gas chromatography. During the reaction a terminal sulfide, $\text{Ru}(\text{N})(\text{S})\text{Me}_3^{2-}$, may be generated which could abstract a proton from the solvent or adventitious water to yield the sulfhydryl complex $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_3(\text{SH})]$, **2** (Scheme 1).⁹ The yellow product crystallizes from methylene chloride/ether/hexane in 75% yield.¹⁰ In anhydrous, deuterated solvent (CD_3NO_2 or CD_3CN), the reaction of **1** with chloride or fluoride cleanly generates $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_3(\text{SD})]$.¹¹ Compound **1** also reacts with stoichiometric quantities of water to produce **2** in 42% yield.

Alternatively, complex **2** can be synthesized in 82% yield directly from the reaction between $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_3\text{Br}]$ and NaSH . Complex **2** is stable to H_2O and O_2 , but the sulfhydryl proton readily exchanges with water.

The molecular structure of **2** was determined by single-crystal X-ray diffraction (Figure 1).¹² The complex has a distorted square pyramidal structure around the ruthenium center with a nitrido ligand, a sulfhydryl ligand, and three methyl groups. The bond angles and distances within the $(\text{N})\text{RuMe}_3$ moiety are very similar to those in $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_4]$.¹³ The Ru–N distance of 1.595(6) Å in **2** is slightly longer than the Ru–N distance of 1.58(1) Å in $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_4]$. More importantly, $\nu_{\text{Ru}=\text{N}}$ is 6 cm^{-1} lower in **2** than in $[\text{PPh}_4][\text{Ru}$

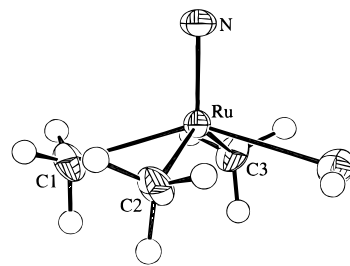


Figure 1. ORTEP diagram of **2**. There is 4-fold symmetry on the crystal due to disorder between atoms C1 and S. The sulfhydryl H atom was independently refined. Selected bond distances (Å) are as follows: Ru–N = 1.595(6), Ru–Cl = 2.19(2), Ru–S = 2.26(2), S–H = 1.1(2). Selected bond angles (deg) are as follows: N–Ru–Cl = 109.1(5), Cl(#1)–Ru–Cl(#2) = 83.8(3), Cl(#1)–Ru–Cl(#3) = 141.7(10), Cl(#2)–Ru–S = 145.2(2), Cl(#1)–Ru–S = 86.8(10), Ru–S–H = 100(10).

(N) Me_4), suggesting that the sulfhydryl ligand is a better donor ligand than the methyl ligand. The N–Ru–C angle of $109.1(5)^\circ$ matches closely to that of 110.4° in $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_4]$. The C–Ru–C angle in **2** of $83.8(3)^\circ$ is also close to the value of 83.0° in $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_4]$. The average Ru–C distance in **2** of 2.19 Å is significantly longer than 2.14 Å of $[\text{PPh}_4][\text{Ru}(\text{N})(\text{Me})_4]$ due to disorder between the methyl and sulfhydryl ligands.

Only a handful of structurally-determined ruthenium sulfhydryl complexes have been reported.¹⁴ Complex **2** is the first Ru(VI) sulfhydryl complex. The sulfhydryl H atom was independently refined, and the Ru–S–H angle is $100(10)^\circ$, close to the value of 99° reported for one of the Ru–S–H angles in $\text{Ru}(\text{SH})_2(\text{CO})_2(\text{PPh}_3)_3$.¹⁴ The S–H distance of 1.1(2) Å is close to the reported values ranging from 1.0 to 1.2 Å.¹⁵ The Ru–S bond length of 2.26(2) Å of **2** as compared to the various Ru–S distances reported ranging from 2.44 to 2.47 Å is not only consistent with the smaller radius of the Ru(VI) center as compared to Ru(II) of the various reported ruthenium sulfhydryl complexes but also can be attributed to the disorder in the crystal of **2**.

The generation of transition metal terminal sulfide and oxide complexes via α -elimination reactions of metal sulfhydryl and hydroxyl complexes has been previously reported by Bergman and co-workers.¹⁶ We cannot isolate a terminal sulfide from **2**. Instead, thermolysis of this complex at 75°C for 12 h in dry CD_3CN in an NMR tube quantitatively converts it to $[\text{PPh}_4][\{\text{Ru}(\text{N})\text{Me}_2\}_3(\mu_3\text{S})_2]$ (Scheme 2).⁶ The previously reported triruthenium sulfido complex may form by the aggregation of “ $\text{Ru}(\text{N})\text{Me}_2\text{S}^-$ ” units and subsequent elimination of S^{2-} .

Complex **1** reacts with a variety of transition metal chlorides to generate chlorotrimethylsilane as deter-

(8) ^1H NMR (400 MHz, CDCl_3 , 20.5°C): δ 7.92 (m, 4 H, *p*- PC_6H_5), 7.77 (m, 8 H, *o*- PC_6H_5), 7.60 (m, 8 H, *m*- PC_6H_5), 1.05 (s, 6 H, *cis*- RuCH_3), 1.04 (s, 3 H, *trans*- RuCH_3), 0.35 (s, 9 H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3 , 20.3°C): 135.8 (d, $J = 3\text{ Hz}$, *p*- PC_6H_5), 134.4 (d, $J = 11\text{ Hz}$, *o*- PC_6H_5), 130.8 (d, $J = 12\text{ Hz}$, *m*- PC_6H_5), 117.4 (d, $J = 90\text{ Hz}$, *ipso*- PC_6H_5), 9.9 (s, *cis*- RuCH_3), 8.1 (s, *trans*- RuCH_3), 6.03 (s, SiCH_3). IR (KBr pellet, cm^{-1}): 3046–2877 (s, ν_{CH}), 1576 (m, $\nu_{\text{C}=\text{C}}$), 1484 (s, δ_{CH}), 1436 (vs, $\nu_{\text{C}=\text{C}}$), 1236 (s, δ_{SiC}), 1074 (vs, ν_{RuN}), 834 (s, ν_{SiC}), 723 (vs, δ_{CH}), 688 (vs, δ_{oopCH}), 527 (vs, δ_{oopCH}). Anal. Calcd for $\text{RuC}_{30}\text{H}_{38}\text{NPSi}$: C, 59.49; H, 6.33; N, 2.31, S, 5.28, Si, 4.62. Found: C, 59.24; H, 6.21; N, 2.54, S, 5.08; Si, 4.44.

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(10) ^1H NMR (400 MHz, CDCl_3 , 20.5°C): δ 7.92 (m, 4 H, *p*- PC_6H_5), 7.77 (m, 8 H, *o*- PC_6H_5), 7.60 (m, 8 H, *m*- PC_6H_5), 1.02 (s, 3 H, *trans*- RuCH_3), 0.94 (s, 6 H, *cis*- RuCH_3), -0.64 (s, 1 H, RuSH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3 , 20.3°C): 135.8 (d, $J = 3\text{ Hz}$, *p*- PC_6H_5), 134.4 (d, $J = 11\text{ Hz}$, *o*- PC_6H_5), 130.8 (d, $J = 12\text{ Hz}$, *m*- PC_6H_5), 117.4 (d, $J = 90\text{ Hz}$, *ipso*- PC_6H_5), 8.3 (s, *cis*- RuCH_3), 6.2 (s, *trans*- RuCH_3). IR (KBr pellet, cm^{-1}): 3059–2870 (s, ν_{CH}), 2521 (m, ν_{SH}), 1577 (m, $\nu_{\text{C}=\text{C}}$), 1483 (s, δ_{CH}), 1437 (vs, $\nu_{\text{C}=\text{C}}$), 1073 (vs, ν_{RuN}), 756 (vs, δ_{CH}), 689 (vs, δ_{oopCH}), 527 (vs, δ_{oopCH}). Anal. Calcd for $\text{RuC}_{27}\text{H}_{30}\text{NPS}$: C, 60.78; H, 5.67; N, 2.63. Found: C, 60.38; H, 5.68; N, 2.77.

(11) IR (KBr pellet): $\nu_{\text{SD}} = 1830\text{ cm}^{-1}$; $\nu_{\text{SH}}/\nu_{\text{SD}} = 1.38$.

(12) Data were measured on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SHELXS-86). Crystallographic data for **2** (198 K): space group $P4/n$; molecules per unit cell (Z) = 2; cell dimensions $a = 13.267(2)\text{ Å}$, $b = 13.267(2)\text{ Å}$, $c = 7.210(2)\text{ Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$; $V = 1269.1(4)\text{ Å}^3$, $Z = 2$; $R = 0.0328$, $R_w = 0.0392$ for 1221 observed reflections.

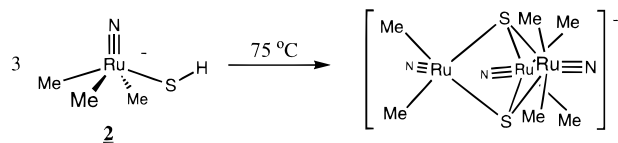
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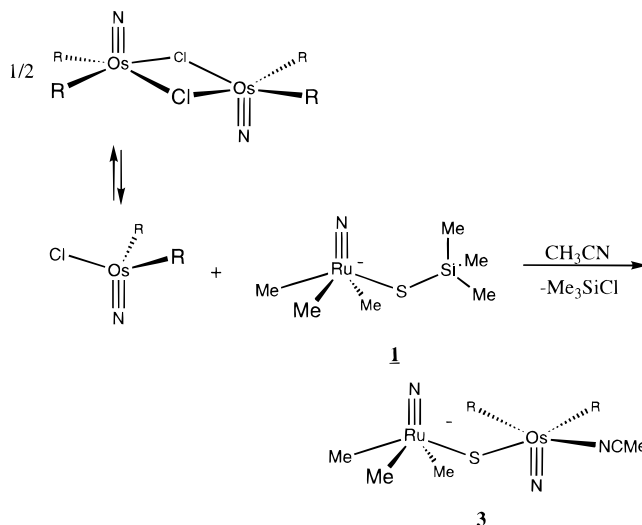
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Scheme 2



Scheme 3



mined by gas chromatography. The reaction of $1/2$ equivalent of $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-Cl})_2]$ with **1** in acetonitrile produces $[\text{PPh}_4][(\text{Me}_3\text{SiCH}_2)_2\text{NCMe}(\text{N})\text{Os}(\mu\text{-S})\text{Ru}(\text{N})\text{Me}_3]$, **3**, and 1 equiv of Me_3SiCl .¹⁷ The significantly lowered Os–nitride stretch in **3** compared with that of the starting material indicates the presence of a strong donor ligand such as sulfur on the osmium center. The ^1H NMR data are consistent with a ruthenium center with two sets of methyl resonances in a 2:1 ratio and an osmium center with an acetonitrile ligand and two inequivalent (trimethylsilyl)methyl ligands.

There is some precedent for this bridge-building reaction. Cai and Holm have reacted an iron triethylsulfanethiolate complex with an Fe(III) octaethylporphyrin fluoride to generate a bridging sulfido bimetallic compound.¹⁸ Doherty and co-workers have also used the loss of trimethylsilyl halides to drive the formation of nitrido-bridged dimers and oligomers in reactions of (trimethylsilyl)imido complexes with metal halides.¹⁹

We have demonstrated that transition metal trimethylsulfanethiolate complexes behave as protected metal sulfides and react readily with a variety of halide sources to cleave the silicon–sulfur bond. The removal of the trimethylsilyl group from **1** by free halides results in the putative formation of a reactive sulfide interme-

diolate and the abstraction of solvent proton to form the sulfhydryl complex **2**. Heating **2** facilitates the α -elimination of methane to form an intermediate which aggregates into a triruthenium μ_3 -sulfido complex. We have also shown that the reactivity of **1** with transition metal halides may be utilized to form sulfur bridges between metal centers.

Acknowledgment. We thank Scott R. Wilson and Teresa Prussak-Wieckowska for obtaining the X-ray structure of $[\text{PPh}_4][\text{Ru}(\text{N})\text{Me}_3(\text{SH})]$. We gratefully acknowledge the financial support of the National Science Foundation for this work (Grant NSF CHE 93-08450). 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).

Supporting Information Available: For $[\text{PPh}_4][\text{Ru}(\text{N})\text{Me}_3(\text{SH})]$, tables of additional crystallographic data, atomic coordinates, thermal parameters, and additional distances and angles and, for $[\text{PPh}_4][\text{Ru}(\text{N})\text{Me}_3\text{Br}]$ and compounds **1–3**, text describing experimental synthetic and X-ray procedures (7 pages). Ordering information is given on any current masthead page.

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(17) ^1H NMR (400 MHz, CDCl_3 , 20.5 °C): δ 7.92 (m, 4 H, *p*- PC_6H_5), 7.77 (m, 8 H, *o*- PC_6H_5), 7.60 (m, 8 H, *m*- PC_6H_5), 3.58 (d, $J = 9$ Hz, 2 H, OsCH^aH^b), 2.75 (d, $J = 9$ Hz, 2 H, OsCH^aH^b), 2.49 (d, $J = 10$ Hz, 2 H, OsCH^cH^d), 2.42 (d, $J = 10$ Hz, 2 H, OsCH^cH^d), 2.12 (s, 3 H, OsNCCH_3), 1.08 (s, 3 H, *trans*- RuCH_3), 0.97 (s, 6 H, *cis*- RuCH_3), 0.09 (s, 9 H, SiCH_3), -0.01 (s, 9 H, SiCH_3). IR (KBr pellet, cm^{-1}): 2942–2868 (s, ν_{CH}), 2317 (w, ν_{CN}), 1603 (m, $\nu_{\text{C-C}}$), 1448 (s, δ_{CH}), 1436 (vs, $\nu_{\text{C-C}}$), 1261 (s, δ_{SiC}), 1240 (s, δ_{SiC}), 1108 (s, ν_{OsN}), 1073 (s, ν_{RuN}), 850 (s, ν_{SiC}), 829 (s, ν_{SiC}), 750 (vs, δ_{CH}), 689 (vs, δ_{oopCH}). Mass spectrum (FAB, 3-NBA and magic bullet, negative ion, m/z): 614 (M^- , $\text{Ru}(\text{N})\text{Me}_3(\mu\text{-S})\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{NCMe})$).

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