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Experimental Data

All reactions were done under nitrogen a N₂ atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres glovebox unless otherwise stated. Anhydrous ether and hexane were distilled from Na/benzophenone. Methylene chloride, acetonitrile, and nitromethane were distilled from CaH₂. Deuterated chloroform was distilled from CaH₂ and dried over molecular sieves. NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a VG ZAB-SE (FAB). All analyses were performed by the University of Illinois microanalytical service.

Preparation of [PPh₄][Ru(N)Me₃Br]. One equivalent of C₅H₅N·HBr (0.017 g, 0.097 mmol) was added all at once to a magnetically stirring yellow solution of [PPh₄][Ru(N)Me₄] (0.050 g, 0.097 mmol) in 15 mL of CH₂Cl₂. Vigorous gas evolution occurred immediately followed by a color change from yellow to light brown. After 2h, the solvent was removed from the solution under vacuum. The dull brown residue was crystallized from hexane/CH₂Cl₂ at -30° C to yield dark orange crystals (0.053 g, 0.092 mmol, 94%). ¹H NMR (400 MHz, CDCl₃, 20.5 °C): δ 7.92 (m, 4 H, p-PC₆H₅), 7.77 (m, 8 H, o-PC₆H₅), 7.60 (m, 8 H, m-PC₆H₅), 1.36 (s, 3 H, *trans*-RuCH₃), 1.20 (s, 6 H, *cis*-RuCH₃). IR (KBr pellet, cm⁻¹): 3064-2874 (s, ν_{CH}), 1586 (m, ν_{C=C}), 1483 (s, δ_{CH}), 1440 (vs, ν_{C=C}), 1080 (vs, ν_{RuN}), 724 (vs, δ_{CH}), 687 (vs, δ_{oopCH}), 527 (vs, δ_{oopCH}). Anal. Calcd. for RuC₂₇H₂₉NPBr: C, 55.96; H, 5.04; N, 2.42. Found: C, 55.79; H, 4.80; N, 2.32.

Synthesis of [PPh₄][Ru(N)Me₃SSiMe₃], **1.** To a magnetically stirred orange solution of [P(C₆H₅)₄][Ru(N)Me₃Br] (0.020 g, 0.035 mmol) in 20 mL of CH₂Cl₂ 1.5 equivalents of NaSSiMe₃ (0.006 g, 0.049 mmol) were added all at once. The suspension of NaSSiMe₃ and **2** was stirred for 30 min, after which the solvent was removed under vacuum. A 1:1 mixture of ether and CH₂Cl₂ was added to the brown residue and the resulting mixture cooled to -30° C for 20 min. The mixture was filtered to yield a bright orange solution. Hexane was added slowly to the solution and the product was crystallized at -30° C to form bright orange crystals (0.013 g, 0.021 mmol, 61 %). ¹H NMR (400 MHz, CDCl₃, 20.5 °C): δ 7.92 (m, 4 H, p-PC₆H₅), 7.77 (m, 8 H, o-PC₆H₅), 7.60 (m, 8 H, m-PC₆H₅), 1.05 (s, 6 H, *cis*-RuCH₃), 1.04 (s, 3 H, *trans*-RuCH₃), 0.35 (s, 9 H, RuSSi(CH₃)₃). ¹³C{¹H} (100 MHz, CDCl₃, 20.3 °C): 135.80 (d, J = 3.0 Hz, p-PC₆H₅), 134.35 (d, J = 10.6 Hz, o-PC₆H₅), 130.79 (d, J = 12.1 Hz, m-PC₆H₅), 117.42 (d, J = 89.5 Hz, *ipso*-PC₆H₅), 9.87 (s, *cis*-RuCH₃), 8.10 (s, *trans*-RuCH₃), 6.03 (s, RuSSi(CH₃)₃). IR (KBr pellet, cm⁻¹): 3046-2877 (s, ν_{CH}), 1576 (m, ν_{C=C}), 1484 (s, δ_{CH}), 1436 (vs, ν_{C=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 RuC₃₀H₃₈NPSSi: 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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Synthesis of [PPh₄][Ru(N)Me₃(SH)], 2. Method A: A solution of 1 (0.005 g, 0.008 mmol) was added to a suspension of 1 equivalent of CsF (0.001 g, 0.008 mmol) in 25 mL of CH₃NO₂ and the mixture was magnetically stirred at room temperature. The color of the solution slowly turned from orange to yellow. After 12 h, the solvent was removed under vacuum and the dull yellow residue was extracted with a 2:1 mixture of CH₂Cl₂/ether and filtered to yield a bright yellow solution. Hexane was added to the solution and the product was crystallized at -30° C to yield yellow needle-like crystals (0.003 g, 0.006 mmol, 75%). **Method B:** To a solution of [PPh₄][Ru(N)Me₃Br] (0.012 g, 0.021 mmol) in 20 mL of THF an excess of NaSH (0.002 g, 0.036 mmol) was added all at once. The cloudy orange solution was stirred for 12 h at room temperature. The solvent was then removed under vacuum and the dull yellow residue was extracted with a 2:1 mixture of CH₂Cl₂/ether and filtered to yield a bright yellow solution. Hexane was added to the solution and the product was crystallized at -30° C to yield yellow needle-like crystals (0.009 g, 0.017 mmol, 82 %). ¹H NMR (400 MHz, CDCl₃, 20.5 °C): δ 7.92 (m, 4 H, p-PC₆H₅), 7.77 (m, 8 H, o-PC₆H₅), 7.60 (m, 8 H, m-PC₆H₅), 1.02 (s, 3 H, *trans*-RuCH₃), 0.94 (s, 6 H, *cis*-RuCH₃), -0.64 (s, 1 H, RuSH). ¹³C{¹H} (100 MHz, CDCl₃, 20.3 °C): 135.80 (d, J = 3.0 Hz, p-PC₆H₅), 134.35 (d, J = 10.6 Hz, o-PC₆H₅), 130.79 (d, J = 12.1 Hz, m-PC₆H₅), 117.42 (d, J = 89.5 Hz, *ipso*-PC₆H₅), 8.32 (s, *cis*-RuCH₃), 6.23 (s, *trans*-RuCH₃). IR (KBr pellet, cm⁻¹): 3059-2870 (s, ν_{CH}), 2521 (m, ν_{SH}), 1577 (m, ν_{C=C}), 1483 (s, δ_{CH}), 1437 (vs, ν_{C=C}), 1073 (vs, ν_{RuN}), 756 (vs, δ_{CH}), 689 (vs, δ_{oopCH}), 527 (vs, δ_{oopCH}). Anal. Calcd. for RuC₂₇H₃₀NPS: C, 60.78; H, 5.67; N, 2.63. Found: C, 60.38; H, 5.68; N, 2.77.

D₂O Proton-Deuterium Exchange Studies of 2. In an NMR tube a sample of 2 was dissolved in CDCl₃. A ¹H NMR spectrum was obtained of the sample. An excess of D₂O (5 μL) was syringed into the NMR tube and the sample was shaken vigorously for 1 min. ¹H NMR spectra of the sample were taken at 10 min intervals for 40 min after the addition of D₂O. The resonance at δ -0.64 ppm assigned to the S-H proton became progressively smaller with respect to the other resonances over 40 min. After 12 h the ¹H NMR spectrum revealed the complete disappearance of the S-H resonance. The IR spectrum also confirmed the disappearance of the resonance at 2521 cm⁻¹ assigned to the S-H stretch and revealed a new resonance at 1830 cm⁻¹ for the S-D resonance.

Synthesis of [PPh₄][(Me₃SiCH₂)₂(NCMe)(N)Os(μ-S)Ru(N)Me₃], 3. To an orange solution of 3 (0.008 g, 0.012 mmol) in 15 mL of CH₂Cl₂ 1/2 equivalent of [Os(N)(CH₂SiMe₃)₂(μ-Cl)]₂ (0.005 g, 0.006 mmol) was added all at once. The orange solution was immediately cooled to -30 °C. After 12 h at -30 °C, the solution had turned dark orange and the solvent was removed under vacuum and the resulting dark orange residue was extracted with ether and filtered to yield a yellow solution. An excess of hexane was added to the solution and the ether was removed under vacuum to leave yellow precipitates in the remaining hexane. The

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yellow solids were filtered off and redissolved in ether and dried to yield yellow solids (0.007 g, 0.007 mmol, 58%). ^1H NMR (400 MHz, CDCl_3 , 20.5 $^\circ\text{C}$): 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, $J = 9.0$ Hz, 2 H, OsCH^aH^b), 2.75 (d, $J = 9.0$ Hz, 2 H, OsCH^aH^b), 2.49 (d, $J = 10.2$ Hz, 2 H, OsCH^cH^d), 2.42 (d, $J = 10.2$ 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, $\text{OsCH}_2\text{Si}(\text{CH}_3)_3$), -0.01 (s, 9 H, $\text{OsCH}_2\text{Si}(\text{CH}_3)_3$). IR (KBr pellet, cm^{-1}): 2942-2868 (s, ν_{CH}), 2317 (w, ν_{CN}), 1603 (m, $\nu_{\text{C}=\text{C}}$), 1448 (s, δ_{CH}), 1436 (vs, $\nu_{\text{C}=\text{C}}$), 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, neg. ion, m/z): 614 (M^- , $\text{Ru}(\text{N})\text{Me}_3\text{R}(\mu\text{-S})\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{NCMe}$).

Crystal data and structure refinement summary for 2.

The prismatic, yellow, translucent cluster data crystal was cut from a cluster and mounted using oil (Paratone-N, Exxon) to a thin glass fiber with the (2 4 -3) scattering planes roughly normal to the spindle axis. There were some crystallites attached to the surface of the crystal. The data crystal was bound by the (1 1 0), (-1 -1 0), (1 -1 -1), (-1 1 1), (0 0 1) and (0 0 -1) faces. Distances from the crystal center to these facial boundaries were 0.05, 0.05, 0.07, 0.07, 0.19, 0.19, 0.21 and 0.21 nm, respectively. Data were measured at 198 K on an Enraf-Nonnius CAD4 diffractometer. Systematic conditions suggested the ambiguous space group $P4/n$; refinement confirmed the presence of a symmetry center. Periodically monitored standard intensities showed no decay. Step-scanned intensity data were reduced by profile analysis and corrected for Lorentz-polarization effects and for absorption. Scattering factors and anomalous dispersion terms were taken from standard tables.

The structure was solved by direct methods; correct positions for Ru and non-H anion atoms were deduced from an E-map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for remaining non-H atoms including disordered positions for atoms C1 and S. Crystallographic 4-fold symmetry was imposed on the anion and 4-bar symmetry was imposed on the cation. The sulfhydryl H atom was independently refined. Methyl H atom positions, Ru-CH_3 , were optimized by rotation about Ru-C bonds with idealized C-H, Ru-H and H-H distances. Remaining H atoms were included as fixed idealized contributors. H atom U's were assigned as 1.2 times U_{eq} of adjacent non-H atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance

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between observed and calculated structure factors showed no dependence on amplitude or resolution.

The proposed model was refined without restraints. Bond length for Ru-C(1) and Ru-S reflect a correlation between disordered positions for atom C(1) and S. The Ru-S bond length is slightly shortened by this correlation and conversely, the Ru-C(1) bond length is slightly lengthened.

Table 1. Crystal Data Collection and Refinement Parameters for **2**

Compound	2
Formula	C ₂₇ H ₃₀ NPRuS
Formula weight	532.62
Space Group	P4/n
<i>a</i> , Å	13.267(2)
<i>b</i> , Å	13.267(2)
<i>c</i> , Å	7.210(2)
$\alpha = \gamma$, deg	90
β , deg	90
Formula/Unit cell, Z	2
Density calculated (ρ) gm/cm ³	1.394
Temperature, K	198 (2)
Radiation	Mo K α (graphite crystal monochromator) K α_1 = 0.70930, K α_2 = 0.71359 K α =0.71071 Å
Absorption Coeff.(μ), mm ⁻¹	0.777
$R = \sum F_o - F_c / \sum F_o $	0.0328
$R_w = (\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$	0.0482
Max. and min. transmission	0.922 and 0.894
Index Ranges	0<= <i>h</i> <=15, 0<= <i>k</i> <=15, -8<= <i>l</i> <=0
Reflections collected	1221
Independent reflections	1120 [R(int) = 0.0392]
F(000)	548
dimensions, mm	0.42 x 0.14 x 0.10

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Table 2. Selected Bond Lengths (Å) for **2**

Ru-N	1.595(6)	Ru-C(1)#1	2.19(2)
Ru-C(1)	2.19(2)	Ru-C(1)#2	2.19(2)
Ru-C(1)#3	2.19(2)	Ru-S	2.26(2)
Ru-S#1	2.26(2)	S-H	1.1(2)
C(1)-H(1A)	0.98	C(1)-H(1B)	0.98
C(1)-H(1C)	0.98	P-C(4)	1.795(3)
P-C(4)#4	1.795(3)	P-C(4)#5	1.795(3)
P-C(4)#6	1.795(3)	C(4)-C(9)	1.388(5)
C(5)-C(6)	1.373(5)	C(5)-H(5)	0.95
C(6)-C(7)	1.385(6)	C(6)-H(6)	0.95
C(7)-C(8)	1.374(6)	C(7)-H(7)	0.95
C(8)-C(9)	1.378(5)	C(8)-H(8)	0.95

Table 3. Selected Bond Angles (deg) for **2**

N-Ru-C(1)	109.1(5)	C(1)#1-Ru-C(1)	83.8(3)
N-Ru-C(1)#2	109.1(5)	C(1)#1-Ru-C(1)#2	83.8(3)
C(1)-Ru-C(1)#2	141.7(10)	N-Ru-C(1)#3	109.1(5)
C(1)#1-Ru-C(1)#3	141.7(10)	C(1)-Ru-C(1)#3	83.8(3)
C(1)#2-Ru-C(1)#3	83.8(3)	N-Ru-S	105.6(4)
C(1)#1-Ru-S	86.8(10)	C(1)-Ru-S	4.0(10)
C(1)#2-Ru-S	145.2(2)	C(1)#3-Ru-S	83.1(10)
N-Ru-S#1	105.6(4)	C(1)#1-Ru-S#1	4.0(10)
C(1)-Ru-S#1	83.1(10)	C(1)#2-Ru-S#1	86.8(10)
C(1)#3-Ru-S#1	145.2(2)	S-Ru-S#1	85.9(2)
Ru-S-H	100(10)	Ru-C(1)-H	106(10)
Ru-C(1)-H(1A)	109.5(5)	H-C(1)-H(1A)	84(10)
Ru-C(1)-H(1B)	109.5(5)	H-C(1)-H(1B)	30(10)
H(1A)-C(1)-H(1B)	109.5	Ru-C(1)-H(1C)	109.5(6)
H(1A)-C(1)-H(1C)	109.5	R(1B)-C(1)-H(1C)	109.5
C(4)-P-C(4)#4	107.2(2)	C(4)-P-C(4)#5	110.63(10)
C(4)#4-P-C(4)#5	110.63(10)	C(4)-P-C(4)#6	110.62(10)
C(4)#4-P-C(4)#6	110.63(10)	C(4)#5-P-C(4)#6	107.2(2)

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C(9)-C(4)-C(5)	120.4(3)	C(9)-C(4)-P	121.4(2)
C(5)-C(4)-P	118.2(2)	C(6)-C(5)-C(4)	119.7(3)
C(6)-C(5)-H(5)	120.2(2)	C(4)-C(5)-H(5)	120.2(2)
C(5)-C(6)-C(7)	120.0(3)	C(5)-C(6)-H(6)	120.0(2)
C(7)-C(6)-H(6)	120.0(2)	C(8)-C(7)-C(6)	120.0(3)
C(8)-C(7)-H(7)	120.0(2)	C(6)-C(7)-H(7)	120.0(2)
C(7)-C(8)-C(9)	121.1(4)	C(7)-C(8)-H(8)	119.5(2)
C(9)-C(8)-H(8)	119.5(2)	C(8)-C(9)-C(4)	118.8(3)
C(8)-C(9)-H(9)	120.6(2)	C(4)-C(9)-H(9)	120.6(2)

Table 4.

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**
(U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x	y	z	U(eq)
Ru	2500	2500	2334(1)	31(1)
S	3226(15)	1027(14)	1490(22)	64(5)
C(1)	3141(17)	1076(14)	1337(24)	52(5)
N	2500	2500	4546(8)	46(2)
P	7500	2500	0	24(1)
C(4)	7730(2)	1436(2)	1478(4)	28(1)
C(5)	7030(3)	1223(3)	2864(4)	36(1)
C(6)	7188(3)	420(3)	4030(5)	45(1)
C(7)	8047(3)	-165(3)	3843(5)	50(1)
C(8)	8740(3)	57(3)	2488(5)	49(1)
C(9)	8594(3)	854(3)	1291(5)	35(1)
H	2565(151)	572(155)	1324(286)	77
H(1A)	3072(30)	1039(17)	-14(23)	63
H(1B)	2781(27)	511(14)	1908(44)	63
H(1C)	3856(19)	1043(21)	1673(58)	63
H(5)	6447(3)	1631(3)	3002(4)	43
H(6)	6709(3)	266(3)	4967(5)	54
H(7)	8156(3)	-720(3)	4651(5)	60
H(8)	9329(3)	-344(3)	2375(5)	59
H(9)	9075(3)	1003(3)	356(5)	42

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Table 5. Anisotropic displacement parameters for **2**.

	<u>U11</u>	<u>U22</u>	<u>U33</u>	<u>U23</u>	<u>U13</u>	<u>U12</u>
Ru	30(1)	30(1)	33(1)	0	0	0
S	83(9)	57(7)	52(5)	11(5)	24(5)	7(5)
C(1)	56(8)	39(8)	61(9)	-26(6)	1(6)	2(6)
N	54(2)	54(2)	30(3)	0	0	0
P	24(1)	24(1)	23(1)	0	0	0
C(4)	37(2)	23(2)	24(2)	0(1)	-7(1)	-5(1)
C(5)	38(2)	39(2)	31(2)	-2(2)	1(1)	-5(1)
C(6)	60(2)	45(2)	30(2)	7(2)	0(2)	-20(2)
C(7)	81(3)	29(2)	41(2)	12(2)	-13(2)	-11(2)
C(8)	67(3)	33(2)	46(2)	4(2)	-10(2)	14(2)
C(9)	40(2)	33(2)	32(2)	1(1)	-2(1)	3(2)