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# Synthesis and structural characterization of complexes of the {Cp\*Rh} and {MeRe} cores with pyridine-2-thiol ligand types. Structures of MeReO( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe)<sub>2</sub> and ( $\eta^5$ -Me<sub>5</sub>C<sub>5</sub>)Rh( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)( $\eta^1$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)

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#### Abstract

Complexes of trimethylsilyl substituted pyridine-2-thiol with rhenium and rhodium have been prepared and structurally characterized. The reaction of methyltrioxorhenium with 3-trimethylsilylpyridine-2-thiol in toluene at 0 °C affords dark green plates of MeReO( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)<sub>2</sub> (4). The reaction of [Cp\*RhCl<sub>2</sub>]<sub>2</sub> with 3-trimethylsilylpyridine-2-thiol in THF, followed by extraction in hexanes and recrystallization yields Cp\*Rh( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)( $\eta^1$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>) (5). Crystal data: 4: monoclinic, P2<sub>1</sub>/c, a=12.898(3), b=13.660(3), c=13.192(3) Å,  $\beta$ =97.58(1)°, V=2303(1) Å<sup>3</sup>, Z=4, D<sub>calc</sub>=1.010 g cm<sup>-3</sup>; structure solution and refinement based on 2297 reflections converged at a conventional residual of 0.0465. 5: orthorhombic, Pna2<sub>1</sub>, a=8.579(2), b=23.315(5), c=15.341(3) Å, V=3068(2) Å<sup>3</sup>, Z=4, D<sub>calc</sub>=1.305 g cm<sup>-3</sup>; 1455 reflections, R=0.0572.

Keywords: Crystal structures; Rhodium complexes; Rhenium complexes; Thiol complexes

### 1. Introduction

In the radiopharmaceutical industry, the incorporation of the <sup>99m</sup>Tc radionuclide into certain diagnostic imaging agents has been performed successfully so that various anatomical features such as the brain, heart, lung, GI tract and kidneys can be imaged with high efficiency on a routine basis [1-6]. More recently, efforts have been made to study other radionuclides whose nuclear properties enable them to be utilized as therapeutic radiopharmaceuticals. Two of these, <sup>186</sup>Re and <sup>105</sup>Rh, have been explored as possible radionuclides to incorporate into therapeutic agents [7–15]. <sup>186</sup>Re is especially promising because: (i) since Re is a congener of Tc, therapeutic rhenium agents can be designed by analogy to existing technetium diagnostic agents and would be expected to have similar biodistribution properties; (ii) the half-life (90 h) and strong  $\beta$ -emission ( $\beta_{max} = 1070 \text{ keV}$ ) enable this radioisotope to deliver high radiation doses to tissue; (iii) <sup>186</sup>Re has a photon emission of approximately the same energy as <sup>99m</sup>Tc ( $\gamma = 137$  keV) which allows the radioisotope to be

imaged by  $\gamma$ -cameras utilized in routine <sup>99m</sup>Tc diagnostic imaging.

Recently we have explored the coordination chemistry of technetium and rhenium organohydrazine complexes to model the uptake of <sup>99m</sup>Tc and <sup>186,188</sup>Re by a bifunctional hydrazine reagent [16–22]. This hydrazine reagent incorporates what is termed the 'metal-tagged' approach in that it links a radionuclide to an antibody and can be subsequently utilized in diagnostic oncological applications and also for the imaging of focal sites of infection [23,24].

Concurrent with the development of novel bifunctional chelates is the development of co-ligands that will aid in the stabilization of these bifunctional chelates. The identity of these co-ligands may profoundly influence structures adopted by complexes possessing {MNNR} or {MNNR<sub>2</sub>} cores [16–22,24–31]. Co-ligands that contain sulfur donor atoms have been particularly effective in the isolation of these complexes due to the high affinity of rhenium and rhodium for sulfur ligands. To this end, we decided to investigate the reactivity of pyridine-2-thiol (1) and a sterically-hindered thiolate ligand 3-trimethylsilylpyridine-2-thiol (2) with the watersoluble metal substrates MeReO<sub>3</sub> and [Cp\*RhCl<sub>2</sub>]<sub>2</sub>

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(Cp<sup>\*</sup> =  $\eta^{5}$ -Me<sub>5</sub>C<sub>5</sub>). The organometallic rhenium complex MeReO<sub>3</sub> has been studied extensively by Herrmann and coworkers and has demonstrated unusual reactivity and catalytic properties in both organic and aqueous solutions [32– 36]. The organometallic rhodium complex, [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub>, has also demonstrated a wealth of reactivity in aqueous solution and has been utilized in biological studies involving nucleotide recognition [37–39]. The products of these reactions, MeReO( $\eta^{2}$ -2-SC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub> (3), MeReO( $\eta^{2}$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)<sub>2</sub> (4) and Cp<sup>\*</sup>Rh( $\eta^{2}$ -2C<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)( $\eta^{1}$ -2-C<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>) (5), were characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy and in the case of 4 and 5, by X-ray crystallography.

# 2. Experimental

#### 2.1. General considerations

NMR spectra were recorded on a General Electric QE 300 (<sup>1</sup>H 300.10 MHz) spectrometer in  $CD_2Cl_2$  ( $\delta 5.32$ ). Variable temperature <sup>1</sup>H NMR spectra utilized a Doric Trendicator 410A temperature controller. IR spectra were recorded as KBr pellets with a Perkin-Elmer 1600 Series FTIR. Elemental analysis for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY.

All synthetic manipulations were carried out utilizing standard Schlenk techniques and solvents were distilled from their appropriate drying agents [40]. Triethylamine (Aldrich) was distilled from CaH<sub>2</sub> and stored under an inert atmosphere. Pyridine-2-thiol (Aldrich), chlorotrimethylsilane (Petrarch), butyllithium (2.5 M solution in hexanes; Aldrich), Re<sub>2</sub>O<sub>7</sub> (Strem), hexafluoroglutaric acid (Aldrich), tetramethylstannane (Strem), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (Aldrich), toluene (Sure-Seal; Aldrich) and other reagents were used as received without further purification. The reagents 2 [41] and methyltrioxorhenium [42] were synthesized by published procedures.

#### 2.2. Syntheses

#### 2.2.1. $(CH_3)ReO(\eta^2 - 2 - SC_5H_4N)_2$ (3)

Methyltrioxorhenium (0.100 g, 0.40 mmol) and pyridine-2-thiol (0.177 g, 1.60 mmol) were dissolved in 15 ml toluene at 0 °C. The reaction mixture turned from colorless to yellow to emerald green over a period of 2 h. After 2 h, the volume of the reaction mixture was reduced to <5 ml and hexanes was added to precipitate a dark green microcrystalline solid (0.027 g, 0.060 mmol, 15%). *Anal.* Calc. for C<sub>12.25</sub>H<sub>12.25</sub>-N<sub>2.25</sub>OReS<sub>2.25</sub> ( $2 \cdot 0.25C_5H_5NS$ ): C, 31.62; H, 2.65; N, 6.77. Found: C, 31.05; H, 2.17; N, 6.53%. IR (KBr, cm<sup>-1</sup>): 3440 (m), 2963 (w), 1634 (w), 1578 (m), 1439 (w), 1421 (w), 1261 (s), 1090 (s), 1017 (s), 970 (m), 802 (s), 763 (m). <sup>1</sup>H NMR (300 MHz, 243 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.48 (d, 1H), 7.71 ('t', 1H, J=7.9 Hz), 7.63 (d, 1H, J=5.7 Hz), 7.16 ('t', 1H, J=7.7 Hz), 7.09 (d, 2H, J=7.8 Hz), 6.87 (d, 1H, J=8.4 Hz), 6.44 ('t', 1H, J=6.2 Hz), 5.00 (s, 3H).

### 2.2.2. $(CH_3)ReO(\eta^2 - 2 - SC_5H_3N - 3 - SiMe_3)_2$ (4)

Methyltrioxorhenium (0.100 g, 0.40 mmol) and 2 (0.293 g, 1.60 mmol) were reacted as described for 3. Recrystallization of the crude product from toluene/hexanes afforded dark green plates (0.059 g, 0.10 mmol, 25%). *Anal.* Calc. for  $C_{17}H_{27}N_2OReS_2Si_2$ : C, 35.09; H, 4.68; N, 4.81. Found: C, 35.39; H, 4.39; N, 5.10%. IR (KBr, cm<sup>-1</sup>): 3437 (w), 2958 (m), 1560 (m), 1369 (s), 1263 (m), 1213 (w), 1091 (w), 1053 (w), 978 (m), 842 (s), 798 (m), 758 (w). <sup>1</sup>H NMR (300 MHz, 233 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.41 (d, 1H, *J*=5.2 Hz), 7.73 (d, 1H), 7.53 (d, 1H), 7.04 ('t', 1H, *J*=6.5 Hz), 6.39 ('t', 1H, *J*=6.3 Hz), 4.82 (s, 3H), 0.42 (s, 9H), 0.40 (s, 9H).

# 2.2.3. $Cp^*Rh(\eta^2 - 2-SC_5H_3N - 3-SiMe_3)(\eta^1 - 2-SC_5H_3N - 3-SiMe_3)(5)$

To a solution of  $[Cp^*RhCl_2]_2$  (0.100 g, 0.16 mmol) in 15 ml THF was charged a solution of 2 (0.178 g, 0.97 mmol) and Et<sub>3</sub>N (0.098 g, 0.97 mmol) in 5 ml THF via syringe. The orange suspension was heated to reflux and after 2 h, the suspension was cooled, filtered to remove the precipitated triethylamine hydrochloride and the solvent was then removed under reduced pressure. The crude product was extracted with hexanes and the extracts were cooled to -20°C. After several days, red crystalline cubes that were suitable for X-ray diffraction studies precipitated from solution. Yield 0.043 g, 0.09 mmol, 56%. Anal. Calc. for C<sub>26</sub>H<sub>39</sub>N<sub>2</sub>RhS<sub>2</sub>Si<sub>2</sub>: C, 51.80; H, 6.52; N, 4.65. Found: C, 52.09; H, 6.58; N, 4.70%. IR (KBr, cm<sup>-1</sup>): 2954 (m), 2870 (w), 2314 (w), 1654 (w), 1558 (s), 1458 (w), 1367 (s), 1350 (s), 1242 (m), 1134 (s), 1024 (w), 858 (s), 758 (m). <sup>1</sup>H NMR (300 MHz, 233 K,  $CD_2Cl_2$ ):  $\delta$  8.33 (d, 1H, J = 5.3 Hz), 8.13 (d, 1H, J = 6.3 Hz, 7.34 (d, 1H, J = 6.9 Hz), 7.24 (d, 1H, J = 7.0Hz), 6.65 ('t', 1H, J = 4.8 Hz), 6.58 ('t', J = 6.3 Hz), 1.66 (s, 15H), 0.28 (s, 9H), 0.26 (s, 9H).

#### 2.3. X-ray crystallography

Compounds 4 and 5 were studied using a Rigaku AFC5S diffractometer, equipped with a low temperature device. Since the crystals degraded slowly at room temperature, data collection was carried out at 213 K. Crystal stability was monitored using 5 medium intensity reflections in each case, and no significant changes in the intensities of the standard were observed over the course of the data collections. The crystal parameters and other experimental details of the data collections are summarized in Table 1. See also Section 4. Atomic positional parameters are listed in Table 2 and Table 3 for 4 and 5, respectively.

The structures were solved by the Patterson method and refined by full-matrix least-squares. See also Section 4. No anomalies were encountered in the refinements of the structures. Inverting the coordinates of 5 to generate the enantio-

#### Table 1

Summary of X-ray crystallographic data for the structures of MeReO( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)<sub>2</sub> (4) and (Cp<sup>\*</sup>)Rh( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)( $\eta^1$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>) (5)

	4	5
Chemical formula	$C_{17}H_{27}N_2OReS_2Si_2$	C <sub>26</sub> H <sub>39</sub> N <sub>2</sub> RhS <sub>2</sub> Si <sub>2</sub>
Formula weight	581.9	482.2
Space group	$P2_1/c$	Pna2 <sub>1</sub>
a (Å)	12.898(3)	8.579(2)
b (Å)	13.660(3)	23.315(5)
c (Å)	13.192(3)	15.341(3)
α (°)	90.00	90.00
β(°)	97.58(1)	90.00
γ (°)	90.00	90.00
$V(Å^3)$	2303(1)	3068(2)
Z	4	4
D <sub>calc</sub>	1.010	1.305
$\mu$ (cm <sup>-1</sup> ) (Mo K $\alpha$ , $\lambda$ = 0.71073 Å)	55.7	7.87
No. reflections used	2297	1455
R <sup>a</sup>	0.0465	0.0572
R <sub>w</sub> <sup>b</sup>	0.0607	0.0682

<sup>a</sup>  $\Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$ 

<sup>b</sup>  $[\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w|F_{o}|^{2}]^{1/2}.$ 

#### Table 2

Atomic coordinates (  $\times 10^4$  ) and equivalent isotropic displacement coefficients (  $\AA^2 \times 10^3$  ) for 4

	x	у	z	U <sub>eq</sub> <sup>a</sup>
Re(1)	3049(1)	5474(1)	3502(1)	34(1)
S(1)	2652(3)	7132(2)	3082(2)	39(1)
S(2)	3000(3)	3955(2)	4508(3)	40(1)
N(1)	3744(7)	6441(7)	4636(7)	35(3)
N(2)	1951(7)	5484(6)	4692(7)	29(3)
Si(1)	3036(3)	9417(2)	4311(3)	37(1)
Si(2)	1648(3)	2961(3)	6418(3)	34(1)
O(1)	3988(7)	5022(7)	2860(7)	48(3)
C(1)	1653(10)	5032(10)	2550(9)	43(3)
C(2)	3392(9)	7352(8)	4288(8)	30(3)
C(3)	3584(9)	8193(9)	4849(8)	33(3)
C(4)	4175(9)	8094(9)	5812(9)	40(3)
C(5)	4547(10)	7194(9)	6178(10)	44(3)
C(6)	4299(10)	6364(10)	5584(9)	42(3)
C(7)	3439(10)	9614(10)	3008(9)	44(3)
C(8)	3537(12)	10409(10)	5196(10)	56(4)
C(9)	1564(10)	9351(10)	4204(11)	58(4)
C(10)	2081(9)	4592(8)	5109(8)	31(3)
C(11)	1556(9)	4249(8)	5915(9)	30(3)
C(12)	918(8)	4960(8)	6301(8)	28(3)
C(13)	814(9)	5896(9)	5891(8)	33(3)
C(14)	1328(9)	6142(9)	5080(9)	35(3)
C(15)	3002(10)	2664(10)	6971(10)	50(4)
C(16)	1164(9)	2112(9)	5372(9)	39(3)
C(17)	772(12)	2872(11)	7438(11)	62(4)

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

morph resulted in a significantly higher residual, confirming the choice reported. Bond lengths and angles for the structures of 4 and 5 are listed in Tables 4 and 5, respectively. 3. Results and discussion

#### 3.1. Spectroscopic results

### 3.1.1. Pyridine-thiol complexes with

methyltrioxorhenium(VII)

The rhenium complexes 3 and 4 were synthesized by the reaction of MeReO<sub>3</sub> with four equivalents of either 1 or 2 in toluene at 0  $^{\circ}$ C (Eq. (1)):

(Me)ReO<sub>3</sub> + 4 
$$R$$
 toluene  
(Me)ReO<sub>3</sub> + 4  $O^{\circ/2}$  h  
(2-HSC<sub>5</sub>H<sub>3</sub>N-3-R) (1)  
R = H (1)  
R = SiMe<sub>3</sub> (2)  
(Me)ReO(2-SC<sub>5</sub>H<sub>3</sub>N-3-R)<sub>2</sub> + 2 RNH<sub>3</sub>C<sub>5</sub>S-SC<sub>5</sub>H<sub>3</sub>NR + 2 H<sub>2</sub>O  
R = H (3)

 $R = SiMe_3$  (4)

Table 3

Atomic coordinates $(\times 10^4)$	and equivalent isotropic	displacement coeffi-
cients ( $Å^2 \times 10^3$ ) for 5	· ·	•

	x	у	z	U <sub>eq</sub> *
 Rh(1)	9181(1)	- 798(1)	2756	34(1)
Si(1)	9325(7)	1505(2)	3816(4)	50(2)
Si(2)	5824(6)	-1582(2)	5563(4)	46(2)
S(1)	8942(5)	124(2)	3367(3)	46(2)
S(2)	6812(5)	-1047(2)	3488(3)	42(2)
N(1)	12017(16)	8(6)	3526(9)	42(4)
N(2)	9576(15)	-1105(6)	4006(8)	31(4)
C(1)	10794(18)	379(7)	3558(9)	33(4)
C(2)	11028(19)	980(7)	3722(11)	36(5)
C(3)	12538(24)	1173(10)	3846(12)	56(5)
C(4)	13738(25)	801(9)	3799(13)	65(6)
C(5)	13522(24)	233(9)	3629(12)	53(5)
C(6)	10174(32)	2240(10)	4032(17)	103(9)
C(7)	8187(20)	1545(8)	2797(15)	64(5)
C(8)	7938(22)	1317(9)	4720(12)	58(6)
C(9)	8156(19)	-1214(7)	4333(10)	31(4)
C(10)	7861(19)	-1423(7)	5142(10)	36(5)
C(11)	9196(20)	-1519(8)	5654(12)	44(5)
C(12)	10701(23)	-1376(8)	5360(12)	54(5)
C(13)	10870(22)	-1175(8)	4520(11)	46(5)
C(14)	4859(26)	-883(8)	5728(13)	62(6)
C(15)	5984(26)	- 1966(9)	6601(13)	77(7)
C(16)	4766(22)	-2035(7)	4782(12)	52(5)
C(17)	10674(21)	- 570(8)	1602(11)	46(5)
C(18)	11188(22)	-1088(9)	1987(13)	52(5)
C(19)	9855(23)	-1502(8)	1914(11)	47(5)
C(20)	8600(23)	- 1219(8)	1535(12)	45(5)
C(21)	9066(19)	-632(7)	1392(11)	38(4)
C(22)	11521(26)	-44(9)	1435(15)	72(6)
C(23)	12752(25)	- 1240(10)	2290(14)	89(8)
C(24)	9954(28)	-2134(9)	2168(15)	79(7)
C(25)	7030(23)	-1475(9)	1296(14)	70(6)
C(26)	8105(24)	- 191(9)	948(12)	67(7)

<sup>a</sup> Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

$\frac{1}{\operatorname{Re}(1)-S(1)}$	2.371(3)	Re(1)-S(2)	2.469(3)	
Re(1) - N(1)	2.106(9)	Re(1)-N(2)	2.249(10)	
Re(1) - O(1)	1.684(9)	$\operatorname{Re}(1)$ -C(1)	2.142(12)	
S(1)-Re(1)-S(2)	155.3(1)	S(1)-Re(1)-N(1)	68.0(3)	
S(2)-Re(1)-N(1)	100.6(3)	S(1)-Re(1)-N(2)	91.2(2)	
S(2)-Re(1)-N(2)	64.3(2)	N(1)-Re(1)-N(2)	75.4(3)	
S(1)-Re(1)-O(1)	112.4(3)	S(2)-Re(1)-O(1)	91.9(3)	
N(1)-Re(1)-O(1)	108.7(4)	N(2)-Re(1)-O(1)	156.0(4)	
S(1)-Re(1)-C(1)	89.6(4)	S(2)-Re(1)-C(1)	89.9(4)	
N(1)-Re(1)-C(1)	147.1(4)	N(2)-Re(1)-C(1)	81.5(4)	
O(1)-Re(1)-C(1)	101.9(4)	Re(1)-S(1)-C(2)	83.0(4)	

Table 4 Selected bond lengths (Å) and angles (°) for 4

Upon addition of the thiol, the reaction mixture turned from colorless to yellow to green over a period of 2 h. The products were isolated by the addition of hexanes to the reaction mixture at low temperatures to yield dark green crystalline solids in low yield. The low product yields could be attributable in part to the high solubility of these complexes and to redox chemistry resulting in the formation of disulfide and unidentified rhenium reduction products. Elemental analysis for 3 and 4 demonstrate that the ratio of metal to ligand is 1:2 and that consequently the rhenium is in the +5 oxidation state. The excess thiolate is required to reduce Re(VII) of the starting material to Re(V) of the product, with concomitant formation of the disulfide species (Me<sub>3</sub>SiC<sub>5</sub>H<sub>3</sub>NS-SC<sub>5</sub>H<sub>3</sub>NSiMe<sub>3</sub>). While the reaction of MeReO<sub>3</sub> with 4 equiv. of thiophenol was observed to yield CH<sub>3</sub>ReO(SPh)<sub>4</sub>, which underwent subsequent elimination of PhSSPh to give the binuclear Re(V) species [MeReO(SPh)<sub>2</sub>]<sub>2</sub> [43], no Re-(VII) monomer could be isolated from the reaction of MeReO<sub>3</sub> with the pyridine-2-thiol derivatives of this study. The IR spectra for 3 and 4 display one  $\nu$  (ReO) stretch at 970 (3) and 978 (4)  $\text{cm}^{-1}$ , indicative of either one rhenium-oxo bond or two rhenium-oxo bonds in a trans orientation [43]. Also, an intense  $\nu$  (Si–C) stretch is observed in 4 at 842 cm<sup>-1</sup> for the organosilyl substituent on the pyridine-thiol ligand. <sup>1</sup>H NMR spectra at 293 K for 3 and 4 consist of broadened resonances for the pyridine-thiolate ligand, indicating that exchange processes between the pyridine-thiolate ligands were occurring in solution at this temperature. At lower temperatures, the slow exchange 'static' spectrum was observed which exhibits two resonances in the trimethylsilyl region for 4, a singlet at  $\delta$  4.82 (3) and 5.00 (4) for the methyl ligand and two sets of aromatic resonances for the pyridyl rings of coordinated 1 and 2. The methyl resonances are shifted unusually far downfield in comparison to other MeReO<sub>3</sub>derived complexes with thiolate ligands (range  $\delta 2.84-3.29$ ) [43]. The two sets of pyridyl resonances observed in the <sup>1</sup>H NMR spectrum demonstrate that the pyridine-thiolate ligands are therefore inequivalent. The structure of 4 was proven unambiguously by X-ray crystallography (vide infra). In consideration of the spectroscopic data for 3, different isomers could be assigned for 3:



Due to electronic considerations, the pyridyl N-donor atoms usually occupy positions *trans* to a strongly bonding oxo group, thus minimizing competition between oxo groups and the weakly  $\pi$ -donating thiolate S-donors for the Re  $t_{2g}$ orbital [40]. Therefore, isomers **3B** and **3C** can be tentatively ruled out. Isomers **3A** and **3D** are the most likely conformations for **3** with **3D** being favored due to it being structurally analogous to **4**.

# 3.1.2. $Cp^* Rh(\eta^2 - 2 - SC_5H_3N - 3 - SiMe_3)(\eta^1 - 2 - SC_5H_3N - 3 - SiMe_3)$

This complex was prepared by the bridge-cleavage reaction of the dimer  $[Cp^*RhCl_2]_2$  with excess 2 in the presence of Et<sub>3</sub>N in refluxing THF (Eq. (2)):

$$(Cp^*)_2 Rh_2 Cl_4 + 4 2 - HSC_5 H_3 N - 3 - SiMe_3$$

$$+ 4Et_3 N \xrightarrow{\text{THF}}_{\Delta/2 \text{ h}} 2Cp^* Rh(2 - SC_5 H_3 N - 3 - SiMe_3)_2$$

$$+ 4Et_3 NHCl \qquad (2)$$

After filtration of the orange suspension to remove precipitated triethylammonium salts, the filtrate was stripped to a crude residue and the product was purified by recrystallization from hexanes at -20 °C to yield red crystalline cubes. Elemental analysis for 5 confirmed that the Cp\*Rh:ligand ratio was 1:2 and IR spectroscopy exhibited an intense  $\nu$ (SiC) at 858 cm<sup>-1</sup> for the organosilyl substituent on 2. <sup>1</sup>H NMR spectroscopy of 5 at 293 K consists of broadened resonances for the pyridine-thiolate ligands, indicative of exchange processes occurring in solution at this temperature. At the slow exchange limit (233 K), two resonances are observed for the trimethylsilyl protons of the coordinated pyridine-thiolate ligands, a large singlet at  $\delta$  1.66 for the methyl protons of the Cp\* ligand and two sets of pyridyl resonances in the aromatic region, demonstrating that the pyridine-thiolate ligands are inequivalent. The structure of 5

Table 5			
Selected bond lengths	(Å)	and angles	(°) for 5

Rh(1)-S(1)	2.354(5)	Rh(1)-S(2)	2.394(4)	
Rh(1)-N(2)	2.074(13)	Rh(1)-C(17)	2.249(18)	
Rh(1)-C(18)	2.194(19)	Rh(1)-C(19)	2.167(18)	
Rh(1)-C(20)	2.173(19)	Rh(1)-C(21)	2.130(17)	
S(1)-Rh(1)-S(2)	87.7(2)	S(1)-Rh(1)-N(2)	87.8(4)	
S(2)-Rh(1)-N(2)	67.7(4)	S(1)-Rh(1)-C(17)	98.5(5)	
S(2)-Rh(1)-C(17)	155.5(5)	N(2)-Rh(1)-C(17)	135.8(6)	
S(1)-Rh(1)-C(18)	124.3(5)	S(2)-Rh(1)-C(18)	147.6(5)	
N(2)-Rh(1)-C(18)	105.2(6)	C(17)-Rh(1)-C(18)	37.1(7)	
S(1)-Rh(1)-C(19)	162.2(5)	S(2)-Rh(1)-C(19)	108.8(5)	
N(2)-Rh(1)-C(19)	104.3(6)	C(17)-Rh(1)-C(19)	63.8(7)	
C(18)-Rh(1)-C(19)	40.3(7)	S(1)-Rh(1)-C(20)	137.4(5)	
S(2)-Rh(1)-C(20)	95.7(5)	N(2)-Rh(1)-C(20)	132.7(6)	
C(17)-Rh(1)-C(20)	63.8(7)	C(18)-Rh(1)-C(20)	65.0(7)	
C(19)-Rh(1)-C(20)	37.4(7)	S(1)-Rh(1)-C(21)	102.8(5)	
S(2)-Rh(1)-C(21)	117.7(5)	N(2)-Rh(1)-C(21)	168.0(6)	
C(17)-Rh(1)-C(21)	37.8(6)	C(18)-Rh(1)-C(21)	64.2(7)	
C(19)-Rh(1)-C(21)	64.2(6)	C(20)-Rh(1)-C(21)	39.1(7)	

where one of the two pyridine-thiolate ligands is chelating and the other pyridine-thiolate ligand is coordinated in a monodentate fashion was confirmed by X-ray crystallography (vide infra).

# 3.2. X-ray crystallographic studies

#### 3.2.1. MeReO( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3SiMi<sub>3</sub>)(<sub>2</sub> (4)

The structure of 4, as shown in Fig. 1, consists of discrete mononuclear units with the Re center in a distorted octahedral environment. The Re coordination geometry {ReCOS<sub>2</sub>N<sub>2</sub>} is defined by the methyl carbon, the terminal oxo group, and the sulfur and nitrogen donors of two 3-trimethylsilylpyridine-2-thiolate ligands in the  $\eta^2$  coordination mode. The structure of 4 establishes the Re(V) oxidation state and confirms that the 4:1 thiolate:Re stoichiometry of the reaction is required to provide sufficient reducing equivalents to form the Re(V) product.

As anticipated the weakly  $\pi$ -bonding thiolate sulfur groups adopt the *trans* orientation. The average Re–S bond length of 2.420(6) Å is significantly longer than the range of 2.28– 2.33 Å previously reported for the Re(V) thiolate species [MeReO(SPh<sub>2</sub>]<sub>2</sub> [43], ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(3,4-S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-1-CH<sub>3</sub>)<sub>2</sub> [36] and [ReO(SPh)<sub>4</sub>]<sup>1-</sup> [44,45]. The Re–S distance is,



Fig. 1. A view of the structure of MeReO( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)<sub>2</sub> (4).

however, similar to that observed for the  $\eta^2$ -coordinated pyridine-2-thiolate ligands of [ReO( $\eta^2$ -SC<sub>5</sub>H<sub>4</sub>N)-( $\eta^1$ -SC<sub>5</sub>H<sub>4</sub>N)] [46] of 2.421(6) Å, an observation which suggests that M–S bond lengthening in complexes containing  $\eta^2$ -coordinated pyridine-2-thiolate groups is a consequence of chelate ring formation and of the steric constraints imposed by coordination to the sp<sup>2</sup> hybridized pyridyl nitrogen. The structural consequences of chelate ring formation involving heterodonors are most obvious in the S–Re–N chelate angles of 68.0(3)° in 4, compared to an average of 73.5° in [MeReO(SPh)<sub>2</sub>]<sub>2</sub>.

The significant lengthening of the Re--N1 distance compared to Re--N2, 2.25(1) versus 2.109(9) Å, reflects the strong *trans* influence of the multiply-bonded oxo group. The Re-O and Re-C bond lengths are in the normal range for multiple and single bonds, respectively [47].

# 3.2.2. $Cp^*Rh(\eta^2 - 2-SC_5H_3N - 3-SiMe_3)(\eta^1 - 2-SC_5H_3N - 3-SiMe_3)_2$

As shown in Fig. 2, the structure of 5 consists of discrete monomers, with a formally six-coordinate Rh(III) center. The 3-trimethylsilylpyridine-2-thiol ligands adopt the two common coordination modes, bidentate through the S and N donors and monodentate through the S donor. Both electronic and steric arguments would favor the observed coordination. The average Rh–S bond distance of 2.374(7) Å is similar to that observed for  $[Cp^*Rh(SC_6F_5)_3]^{1-}$  [48], 2.414(15) Å. The average Rh–C distance of 2.18(2) Å is unexceptional. The major structural distortion is the S2–Rh–N2 valence angle of  $67.7(4)^\circ$ , which is a consequence of five-membered chelate ring formation.

Although both binuclear, thiolate bridged species and mononuclear, tris-thiolate complexes with the  $\{Cp^*Rh\}^{2+}$  core have been described [48], attempts to isolate an analogous species with the sterically hindered-3-trimethylsilylpyridine-2-thiol ligand proved unsuccessful. This observation presum-



Fig. 2. A view of the structure of Cp\*Rh( $\eta^2$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>)( $\eta^1$ -2-SC<sub>5</sub>H<sub>3</sub>N-3-SiMe<sub>3</sub>) (5).

ably reflects the steric constraints imposed by the presence of the trimethylsilyl group on the ring carbon adjacent to the sulfur-bearing carbon [49].

#### 4. Supplementary material

A complete description of the crystallographic methods and details of the structure solutions and refinements are available from the authors on request.

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