

## Synthesis of Dinuclear Rhenium(VI) Oxo-Sulfido Compounds

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Reaction of the  $d^1-d^1$  dimer  $\text{syn}[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  in pyridine with 1 equiv of  $\text{H}_2\text{S}$  at 0 °C for 2 h gave  $\text{syn-Re}_2(\mu\text{-O})(\mu\text{-S})\text{O}_2(\text{CH}_2\text{CMe}_3)_4$  in 86% yield. With 2 equiv of  $\text{H}_2\text{S}$  at 23 °C, a mixture of golden yellow  $\text{syn}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  and red  $\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  was produced (total yield 76%). The red anti isomer was isolated from the mixture by low-temperature fractional crystallization from toluene; crystals of the isomers were also separated mechanically. Gentle heating (40 °C) of  $\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  in pyridine gave  $\text{syn}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  in 88% yield. The isomerization was reversible in pyridine solvent. In NMR experiments,  $\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  was converted to the syn isomer in benzene- $d_6$  at 23 °C in 2 weeks, but the isomerization was accompanied by decomposition. Addition of a trace of bipyridine to the benzene- $d_6$  solution resulted in a faster (2 days at 23 °C) and cleaner (>90% yield by  $^1\text{H}$  NMR integration) anti to syn isomerization. A  $d^1$   $\text{Re}(\text{O})(\text{S})(\text{CH}_2\text{CMe}_3)_2$  intermediate in the isomerization is proposed. The syn and anti isomers of  $[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  were characterized by X-ray crystallography. In each case the rhenium centers have approximately square-pyramidal geometries with the oxo ligands in the apical positions. The syn isomer has virtual  $C_{2v}$  symmetry and the anti  $C_{2h}$  symmetry. The Re-Re distances are 2.759 (3) Å (syn) and 2.871 (2) Å (anti). Crystal data for the syn form of  $\text{Re}_2\text{S}_2\text{O}_2\text{C}_{20}\text{H}_{44}$  at -20 (1) °C: monoclinic, space group  $C2$ ,  $a = 23.82$  (1) Å,  $b = 5.788$  (5) Å,  $c = 19.124$  (8) Å,  $\beta = 98.47$  (2)°,  $Z = 2$ . Crystal data for the anti form of  $\text{Re}_2\text{S}_2\text{O}_2\text{C}_{20}\text{H}_{44}$  at -79 (1) °C: monoclinic, space group  $P2_1/n$ ,  $a = 13.453$  (3) Å,  $b = 6.234$  (2) Å,  $c = 14.949$  (3) Å,  $\beta = 94.50$  (2)°,  $Z = 2$ .

## Introduction

Compounds that contain the  $d^1-d^1$   $[\text{M}_2(\mu\text{-E})_2\text{E}'_2]$  core, where  $\text{E} = \text{E}' = \text{O}$  or  $\text{S}$  and  $\text{E} = \text{S}$  and  $\text{E}' = \text{O}$ , have either a syn or an anti geometry (I and II, respectively). Only in a few cases



have both isomers been observed for a given metal and ligand set.<sup>1</sup> Two of the most well-studied isomer pairs of this type are  $\text{syn}/\text{anti}[\text{M}(\mu\text{-O})(\text{O})\text{L}]_2^{2+}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{L} = 1,4,7\text{-triazacyclononane}$ ) described by Wiegardt and co-workers.<sup>1a</sup> For both pairs, the syn form is thermodynamically more stable, and the anti to syn irreversible isomerization is acid ( $\text{M} = \text{Mo}, \text{W}$ ) or base ( $\text{M} = \text{Mo}$ ) catalyzed.<sup>1a</sup>

Herein we report the synthesis of  $\text{syn-Re}_2(\mu\text{-O})(\mu\text{-S})\text{O}_2(\text{CH}_2\text{CMe}_3)_4$  and the syn and anti isomers of  $[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$ . Both isomers of  $[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  were characterized by X-ray crystallography. We show that  $\text{syn}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  is thermodynamically more stable than the anti form in solution and that the anti to syn isomerization occurs in hydrocarbon solution in the absence of added base or acid.

## Experimental Section

All reactions were carried out under an atmosphere of nitrogen or argon in dry and oxygen-free solvents. The compound  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  was prepared from  $\text{ReO}_3(\text{OSiMe}_3)$  and  $\text{Al}(\text{CH}_2\text{CMe}_3)_3$  as described previously.<sup>2</sup>

$\text{Re}_2(\mu\text{-O})(\mu\text{-S})\text{O}_2(\text{CH}_2\text{CMe}_3)_4$ .  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (0.213 g, 0.30 mmol) was dissolved in pyridine (20 mL) and the greenish yellow solution frozen with liquid nitrogen.  $\text{H}_2\text{S}$  (1.15 equiv, 0.34 mmol) was then condensed into the reaction flask via a calibrated vacuum manifold. The mixture was warmed to 0 °C and stirred at this temperature for 2 h. The color gradually changed to orange-red. The volatiles were then removed in vacuo, and the residue was redissolved in hexane. The resulting orange-red solution was chromatographed on  $\text{Al}_2\text{O}_3$  (neutral, activity grade V) with hexane as eluting solvent. A single band (yellow) was observed and collected and the solvent removed in vacuo. The solids were redissolved in a mixture of toluene and acetonitrile, and the solution was slowly cooled to -20 °C. This produced yellow needles, which were isolated by decanting the supernatant via cannula. The crystals were dried in vacuo (yield 0.187 g, 86%). Anal. Calcd for  $\text{Re}_2\text{S}_2\text{O}_2\text{C}_{20}\text{H}_{44}$ : C, 32.59; H, 6.01; S, 4.35. Found: C, 32.74; H, 5.70; S, 4.37.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.65 and 3.57 (d of an AB q, 4,  $J_{\text{HH}} = 11.9$  Hz,  $\text{CH}_2\text{CMe}_3$ ),

3.60 and 3.21 (d of an AB q, 4,  $J_{\text{HH}} = 10.8$  Hz,  $\text{CH}_2\text{CMe}_3$ ), 1.51 (s, 18,  $\text{CH}_2\text{CMe}_3$ ), 1.43 (s, 18,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  74.2 (s,  $\text{CH}_2\text{CMe}_3$ ), 63.3 (s,  $\text{CH}_2\text{CMe}_3$ ), 37.7 (s,  $\text{CH}_2\text{CMe}_3$ ), 37.6 (s,  $\text{CH}_2\text{CMe}_3$ ), 33.9 (s,  $\text{CH}_2\text{CMe}_3$ ), 33.6 (s,  $\text{CH}_2\text{CMe}_3$ ). IR (Nujol, CsI,  $\text{cm}^{-1}$ ):  $\nu(\text{Re}=\text{O})$  1020 s and 1006 s,  $\nu(\text{Re}-\text{O}-\text{Re})$  744 m and 601 w.

$\text{syn}/\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$ .  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (0.286 g, 0.40 mmol) was dissolved in pyridine (20 mL), and the greenish yellow solution was frozen with liquid nitrogen.  $\text{H}_2\text{S}$  (2.2 equiv, 0.88 mmol) was then condensed into the reaction flask via a calibrated vacuum manifold. The mixture was warmed to room temperature and stirred for 4 h. The color gradually changed to deep red, with formation of an orange-red powder. The volatiles were then removed under vacuum, and the residue was redissolved in toluene. The red solution was chromatographed on  $\text{Al}_2\text{O}_3$  (neutral, activity grade V) with toluene as eluting solvent. A single band (orange) was observed and collected. The volume of the toluene solution was reduced (to 5 mL) in vacuo. Slow cooling to -20 °C produced red needles (anti isomer), which were isolated by decanting the supernatant via cannula. The crystals were dried in vacuo (yield of anti isomer 0.175 g, 59%). The orange supernatant was reduced to 2 mL in volume and then cooled slowly to -80 °C. This produced a mixture of red and golden yellow (syn isomer) crystals, which were isolated by removing the supernatant via cannula. The crystals were dried in vacuo (0.050 g, 17%). The total yield of  $[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  was 76%.

Spectroscopic and analytical data for  $\text{syn}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (golden yellow) are as follows. Anal. Calcd for  $\text{Re}_2\text{S}_2\text{O}_2\text{C}_{20}\text{H}_{44}$ : C, 31.90; H, 5.88; S, 8.51. Found: C, 32.09; H, 5.77; S, 8.00.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.77 and 3.68 (d of an AB q, 8,  $J_{\text{HH}} = 11.3$  Hz,  $\text{CH}_2\text{CMe}_3$ ), 1.51 (s, 36,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  64.7 (s,  $\text{CH}_2\text{CMe}_3$ ), 37.7 (s,  $\text{CH}_2\text{CMe}_3$ ), 34.2 (s,  $\text{CH}_2\text{CMe}_3$ ). IR (Nujol, CsI,  $\text{cm}^{-1}$ ):  $\nu(\text{Re}=\text{O})$  1022 s and 1005 s.

Spectroscopic data for  $\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (red) are as follows.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.80 and 3.41 (d of an AB q,  $J_{\text{HH}} = 10.9$  Hz,  $\text{CH}_2\text{CMe}_3$ ), 1.50 (s, 36,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  65.9 (s,  $\text{CH}_2\text{CMe}_3$ ), 37.6 (s,  $\text{CH}_2\text{CMe}_3$ ), 34.4 (s,  $\text{CH}_2\text{CMe}_3$ ). IR (Nujol, CsI,  $\text{cm}^{-1}$ ):  $\nu(\text{Re}=\text{O})$  993 s.

$\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  to  $\text{syn}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  Isomerization. To  $\text{anti}[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (0.125 g) was added pyridine (20 mL). The slurry was stirred at 40 °C in the absence of light for 16 h, which produced a golden yellow solution. The solvent was removed under vacuum and the solid then redissolved in a mixture of

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- (1) (a) Wiegardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491; *Angew. Chem.* **1983**, *95*, 499. Wiegardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94. Hahn, M.; Wiegardt, K. *Inorg. Chem.* **1984**, *23*, 3977. Wiegardt, K.; Guttman, M.; Chaudhuri, P.; Gebert, W.; Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 3151. Schreiber, P.; Wiegardt, K.; Flörke, U.; Haupt, H.-J. *Inorg. Chem.* **1988**, *27*, 2111. (b) Bunzey, G.; Enemark, J. H.; Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 4168. Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682. Chandler, T.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1981**, *20*, 75. (c) Tanner, L. D.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1988**, *27*, 1741.
- (2) Cai, S.; Hoffman, D. M.; Huffman, J. C.; Wierda, D. A.; Woo, H.-G. *Inorg. Chem.* **1987**, *26*, 3693.

**Table I.** Crystal Data for the Syn and Anti Isomers of  $[\text{Re}(\mu\text{-S})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (3)

	<i>syn</i> -3	<i>anti</i> -3
formula	$\text{C}_{20}\text{H}_{44}\text{O}_2\text{S}_2\text{Re}_2$	$\text{C}_{20}\text{H}_{44}\text{O}_2\text{S}_2\text{Re}_2$
<i>a</i> , Å	23.82 (1)	13.453 (3)
<i>b</i> , Å	5.788 (5)	6.234 (2)
<i>c</i> , Å	19.124 (8)	14.949 (3)
$\beta$ , deg	98.47 (2)	94.50 (2)
<i>V</i> , Å <sup>3</sup>	2608 (2)	1249.8 (6)
<i>Z</i>	2	2
$\lambda$ , Å	0.71073	0.71073
space group	$C2$ (No. 5)	$P2_1/n$ (No. 14)
<i>T</i> , °C	-20 (1)	-79 (1)
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.91	2.00
$\mu$ , cm <sup>-1</sup>	95.7	99.8
<i>R</i> ( <i>F</i> <sub>o</sub> )	0.0696	0.0516
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> )	0.0666	0.0514

toluene and acetonitrile. The solution was cooled slowly to -20 °C. This produced golden yellow crystals of the *syn* isomer, which were isolated by decanting the supernatant via cannula. The crystals were dried in vacuo (yield of *syn* isomer based on anti isomer 0.110 g, 88%).

***syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to *anti*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> Isomerization.** *syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.099 g) was dissolved in pyridine (10 mL). The yellow solution was held at -15 °C for 62 days. During this time, red crystals of the *anti* isomer slowly formed. The crystals were isolated by removing the supernatant via a cannula and then dried in vacuo (0.058 g, 59%). *syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.034 g) was recovered from the decanted pyridine solution by removing the solvent in vacuo; thus, the yield of the *anti* isomer was 89% based on the amount of *syn* isomer consumed. Mechanical losses in handling the small quantities of materials in a glovebox probably account for the 7 mg of material lost in the experiment.

**Crystallography.** Crystal data are given in Table I. X-ray data were collected on a Nicolet R3m four-circle diffractometer equipped with an LT-1 low-temperature device. The collection of data was controlled by use of the Nicolet P3 program. Raw diffractometer data were processed with the program XTape (*syn*-3) or XDisk (*anti*-3). The structure was solved by use of the SHELXTL-PLUS package of programs. Drawings were produced with the Nicolet program XP.

In each case, the crystal was attached to a 0.30-mm glass fiber with a minimum amount of silicon grease. The fiber was then mounted on a 1/8 in. diameter brass pin with epoxy glue. The pin was attached to the goniometer head, and the head was then transferred to the diffractometer, where the crystal was immersed in a cold nitrogen stream.

***syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.** The crystals for study were grown by low-temperature crystallization from a saturated acetonitrile solution (-20 °C; 2 days). Removal of the supernatant solution via a cannula yielded golden yellow blocks. The crystals were handled under a nitrogen atmosphere.

The unit cell was indexed by use of 13 reflections obtained from a rotation photograph. A lattice determination suggested a monoclinic cell. Examination of axial photographs confirmed this assignment. The final unit cell parameters were obtained by a least-squares refinement of 24 selected reflections, including 12 Friedel pairs.

The intensities of three check reflections were measured after every 60 reflections; the crystal decayed 6% during the 190 h of data collection. A linear decay correction based on the intensity changes of the check reflections, a semiempirical absorption correction, and Lorentz and polarization corrections were applied to the data.

Systematic absences were consistent with space groups  $C2$ ,  $Cm$ , and  $C2/m$ . Additionally, the  $h0l$  and  $00l$ ,  $l \neq 2n$ , reflections were weak (approximately 10–20 $\sigma$  above background). The distribution of *E* statistics suggested that  $C2$  was the correct space group. Successful solution in the  $C2$  space group confirmed this choice. A Patterson synthesis readily revealed the positions of the rhenium atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atom positions; therefore, the hydrogen atoms were placed on the carbon atoms in calculated positions [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ ;  $d_{\text{C-H}} = 0.96$  Å] for refinement. Refinement was performed to convergence [ $\Delta/\sigma(\text{max}) < 0.014$ ] with this model. The weighting scheme was  $w = [\sigma^2(F) + gF^2]^{-1}$  ( $g = 78 \times 10^{-4}$ ).

A number of semiempirical absorption corrections were attempted. Corrections employing only scans near  $\chi = 270^\circ$  [ABSCOR (public domain) or XEMP (Nicolet)] produced two nonpositive definite thermal ellipsoids (carbon). In the end, an absorption correction (XEMP) based on scans from six reflections in the range  $10^\circ < 2\theta < 36^\circ$  and equivalent

data (the equivalent data were at least 20 $\sigma$  greater than background) was used. This yielded a refined structure with no nonpositive definite atoms.

***anti*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.** The crystals for study were grown by low-temperature crystallization from a saturated acetonitrile solution (-20 °C; 2 days). Removal of the supernatant solution via cannula yielded red blocks. The crystals were handled under a nitrogen atmosphere.

The unit cell was indexed by use of 15 reflections obtained from a rotation photograph. A lattice determination suggested a monoclinic cell. Examination of axial photographs confirmed this assignment. The final unit cell parameters were obtained by a least-squares refinement of 48 selected reflections, including 12 Friedel pairs.

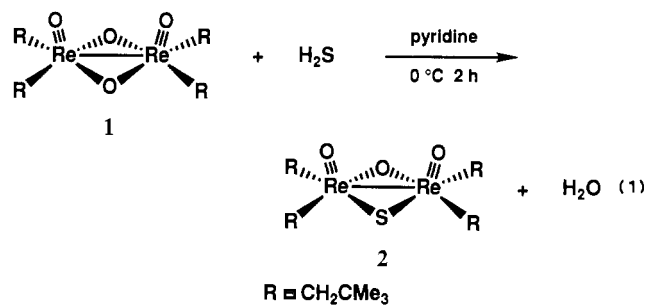
The intensities of three check reflections, which were measured after every 60 reflections, did not change significantly during the 45 h of data collection. A semiempirical absorption correction and Lorentz and polarization corrections were applied to the data.

Systematic absences uniquely determined the space group to be  $P2_1/n$ . A Patterson synthesis readily revealed the position of the rhenium atom. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed most but not all of the hydrogen atom positions; therefore, the hydrogen atoms were placed on the carbon atoms in calculated positions [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ ;  $d_{\text{C-H}} = 0.96$  Å] for refinement. Refinement was performed to convergence [ $\Delta/\sigma(\text{max}) < 0.001$ ] with this model. The weighting scheme was  $w = [\sigma^2(F) + gF^2]^{-1}$  ( $g = 3.5 \times 10^{-4}$ ).

A number of absorption corrections were attempted. Corrections employing only scans near  $\chi = 270^\circ$  [ABSCOR (public domain) or XEMP (Nicolet)] gave one nonpositive definite thermal ellipse and a noisy difference map. An absorption correction (XEMP) based on scans from five reflections in the range  $12^\circ < 2\theta < 33^\circ$  and equivalent data (the intensity of the equivalent data were at least 20 $\sigma$  above background) improved the difference map slightly. An analytical absorption correction eliminated the nonpositive definite atom, but the difference map was still noisy (largest peak 3.5 e Å<sup>-3</sup>). In the end, the program DIFABS with a full set of Friedel pairs was employed. This gave a cleaner difference map (largest peak 2.9 e Å<sup>-3</sup>) and no nonpositive definite atoms. Our absorption correction attempts are summarized in the supplementary material.

## Results and Discussion

**Synthesis and Spectroscopic Characterization.** The reaction at 0 °C of yellow *syn*-[Re( $\mu$ -O)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**1**) with 1 equiv of H<sub>2</sub>S in pyridine for 2 h gave an orange-red reaction mixture. After workup, which included chromatography on Al<sub>2</sub>O<sub>3</sub>, and crystallization from a mixture of toluene and acetonitrile, *syn*-Re<sub>2</sub>( $\mu$ -O)( $\mu$ -S)O<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**2**) was isolated as yellow needles in 86% yield (eq 1).

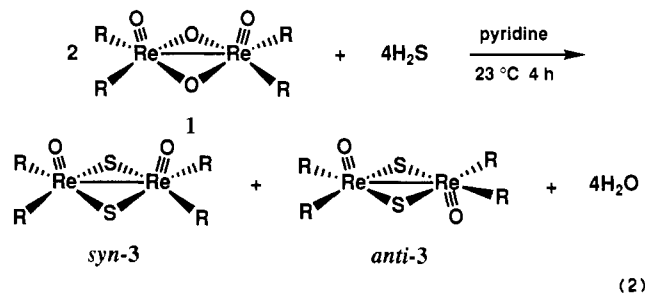


Analytical data for **2** were consistent with the Re<sub>2</sub>SO<sub>3</sub>-(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> formulation. Spectroscopic methods were used to assign the structure. The <sup>1</sup>H NMR spectrum had two singlets of equal intensity in the methyl region and two AB quartets of equal intensity in the methylene region. This was consistent with a *syn* C<sub>2</sub> or *anti* C<sub>2</sub> geometry with a bridging sulfide for **2**. The IR spectrum had bands at 744 (m) and 601 (w) cm<sup>-1</sup>, which were characteristic of a bent M( $\mu$ -O)M moiety (cf. 755 and 514 cm<sup>-1</sup> in **1**).<sup>2,3</sup> There were also strong bands in the Re=O bond region at 1020 and 1006 cm<sup>-1</sup> (cf. 1027 and 1013 cm<sup>-1</sup> in **1**).<sup>2,3</sup> The symmetric and antisymmetric Re=O stretches for both the *syn*

(3) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. Newton, W. E.; McDonald, J. W. *J. Less-Common Met.* **1977**, *54*, 51. Jezowska-Trzebia-towska, B.; Rudolf, M. F.; Natkaniec, L.; Sabat, H. *Inorg. Chem.* **1974**, *13*, 617. Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *8*, 871.

( $C_2$ ) and anti ( $C_2$ ) geometries of **2** are IR active, but the anti geometry is expected to produce a much weaker symmetric stretch because of the effective  $C_i$  symmetry of the  $O=Re-Re=O$  moiety. A comparison of the IR spectra for **1**, which is known to have a syn geometry, and **2** showed there was no significant weakening of either band arising from the  $Re=O$  bonds in the spectrum for **2**. On this basis, a syn geometry for **2** was assigned.

The reaction of **1** in pyridine with 2 equiv of  $H_2S$  at room temperature (eq 2) produced a deep red solution and an orange-red



powder. Chromatography on  $Al_2O_3$  with toluene eluent and subsequent low-temperature crystallization from toluene produced red crystals of *anti*-[ $Re(\mu-S)O(CH_2CMe_3)_2$ ]<sub>2</sub> (*anti-3*) in 59% yield. Reduction of the supernatant toluene solution from this crystallization and slow cooling to  $-80^\circ C$  produced a crystalline mixture of red *anti-3* and golden yellow *syn*-[ $Re(\mu-S)O(CH_2CMe_3)_2$ ]<sub>2</sub> (*syn-3*). The yield from the second crystallization was 17%, for a combined yield of 76% for the syn and anti isomers from the entire procedure. Addition of greater than 2 equiv of  $H_2S$  to **1** gave lower yields of **3** and did not produce trithio or tetrathio compounds.

Due to their striking difference in color (red vs golden yellow), crystalline *syn-3* and *anti-3* could be separated easily with a spatula or tweezers. *syn-3* was extremely soluble in hydrocarbon solvents and pyridine, whereas *anti-3* was less soluble in hydrocarbons and only sparingly soluble in pyridine.

Spectroscopic data collected for *syn-3* and *anti-3* were consistent with the structures shown in eq 2, which were confirmed by X-ray crystallography (see below). For instance, the IR spectrum for *syn-3* showed two strong IR bands at 1022 and 1005  $cm^{-1}$ . These were assigned to the  $A_1$  and  $B_2$   $O=Re-Re=O$  stretches. For *anti-3* there was one strong band in the  $Re=O$  bond region at 993  $cm^{-1}$ . This was assigned to the IR-active  $B_u$   $O=Re-Re=O$  asymmetric stretch; the  $A_g$  symmetric stretch is IR inactive in  $C_{2h}$  symmetry.  $^1H$  NMR spectra for both compounds showed only a singlet in the methyl region and an AB quartet in the methylene region.

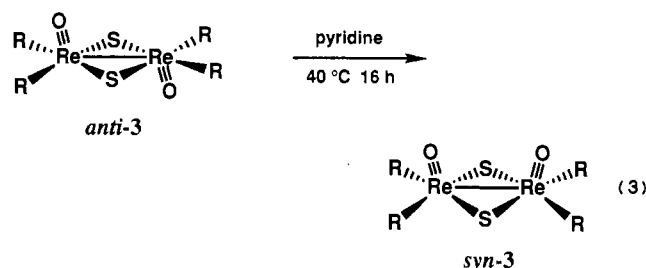
The pyridine solvents used in reactions 1 and 2 were important. As an example, there was no reaction between **1** and 2 equiv of  $H_2S$  in toluene after 8 h at  $23^\circ C$ . The role of pyridine in the reactions is not clear, but two possibilities are (a)  $HS^-$ , which must be present from the equilibrium  $py + H_2S \rightleftharpoons [pyH][SH]$ , is a necessary reagent in the syntheses or (b) pyridine assists in the cleavage of [ $Re(\mu-O)O(CH_2CMe_3)_2$ ]<sub>2</sub> into  $d^1 ReO_2(CH_2CMe_3)_2$  mononuclear fragments, which are in turn more reactive to  $H_2S$  or  $HS^-$  than [ $Re(\mu-O)O(CH_2CMe_3)_2$ ]<sub>2</sub>.

**Anti-Syn Isomerization.** A series of experiments involving *anti-3*→*syn-3* isomerization were carried out. In all of these experiments, light was excluded and the solvents were dry and oxygen-free.

In one experiment, crystals of *anti-3* were dissolved in benzene- $d_6$ , and the isomerization reaction was monitored at  $23^\circ C$  by  $^1H$  NMR spectroscopy (vs  $C_6Me_6$  internal standard). Under these conditions, the anti isomer slowly converted to the syn form in 2 weeks. The isomerization was accompanied by significant decomposition, however, with nearly 50% of **3** lost to decomposition products, which included **1**, **2**, neopentane, and unidentified soluble and insoluble materials.

In contrast to the decomposition observed in benzene, *anti-3* was converted to *syn-3* quantitatively in pyridine- $d_5$  at  $40^\circ C$  in 64 h and, on a laboratory scale, 0.125 g of *anti-3* in pyridine was

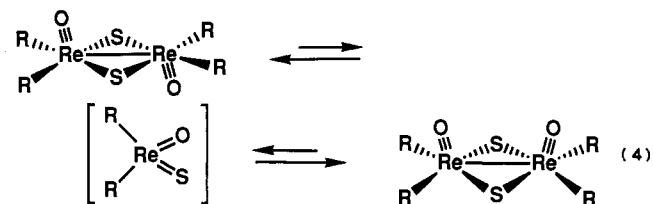
converted to *syn-3* in 88% isolated yield at  $40^\circ C$  in 16 h (eq 3). The faster conversion in the scaled-up experiment was due to the relatively larger volume of pyridine solvent, in which *anti-3* was only sparingly soluble.



Questions about the possible role of pyridine in the isomerization prompted an examination of the isomerization in benzene- $d_6$  with a trace of bipyridine added (0.18 equiv). In this case, the conversion was qualitatively faster (2 days at  $23^\circ C$  vs 2 weeks) and cleaner (>90% vs 50% yield by  $^1NMR$  integration) than when the reaction was carried out in neat benzene.

In the  $^1H$  NMR experiments there was no evidence for reversibility in the *anti-3*→*syn-3* conversion. It was found, however, that when a dilute solution of *syn-3* in pyridine was left at  $-15^\circ C$  for 4 weeks in an NMR tube, red crystals of *anti-3* slowly formed. For an analogous large-scale experiment, *syn-3* was converted to *anti-3* in 89% isolated yield based on the amount of *syn-3* consumed. In these experiments, the crystallization process must draw *anti-3* from a *syn-3* = *anti-3* equilibrium. Thus, the isomerization is in fact reversible, although *syn-3* is thermodynamically more stable than *anti-3* in benzene or pyridine solution and the equilibrium strongly favors *syn-3*.

On the basis of these experiments, we tentatively propose that the mechanism of syn-anti isomerization involves complete disruption of the dimers into mononuclear fragments (eq 4).



Furthermore, because the isomerization was cleaner in pyridine or with added bipyridine than in neat benzene and was qualitatively faster when bipyridine was present, we propose that these coordinating solvents help cleave the dimers and block via coordination decomposition pathways available to the  $Re(O)(S)(CH_2CMe_3)_2$  intermediate. The  $Re(O)(S)(CH_2CMe_3)_2$  intermediate in reaction 4 would be analogous to the  $Re^{VI} ReO_2(aryl)_2$  compounds synthesized and structurally characterized by Wilkinson, Hursthouse, and co-workers.<sup>4</sup>

**Crystallography Studies.** The syn and anti forms of **3** were characterized by single-crystal X-ray diffraction studies. A crystal data summary is given in Table I, selected bond distances and angles are listed in Tables II (*syn-3*) and IV (*anti-3*), and positional parameters are given in Tables III (*syn-3*) and V (*anti-3*).

There are two crystallographically independent molecules in the unit cell for *syn-3*, each of which has crystallographically imposed  $C_2$  symmetry. The important bond distances and angles for the two molecules are not significantly different. An ORTEP plot of one of the independent molecules is presented in Figure 1, and a plot of the other appears in the supplementary material. An ORTEP plot of *anti-3* is presented in Figure 2. Molecules of *anti-3* have a crystallographically imposed center of inversion.

(4) Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 31. Stravropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169. Longley, C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1079.

**Table II.** Selected Bond Distances (Å) and Angles (deg) for One of Two Molecules of *syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*syn*-3) in the Unit Cell<sup>a</sup>

Bond Distances			
Re(1)–S(1)	2.238 (7)	Re(1)–Re(1A)	2.759 (3)
Re(1)–O(1)	1.729 (12)	Re(1)–S(1A)	2.242 (7)
Re(1)–C(1)	2.141 (20)	Re(1)–C(2)	2.165 (24)
Bond Angles			
S(1)–Re(1)–O(1)	114.7 (7)	C(2)–Re(1)–Re(1A)	125.6 (7)
S(1)–Re(1)–C(1)	85.8 (6)	S(1)–Re(1)–S(1A)	99.2 (2)
O(1)–Re(1)–C(1)	99.5 (9)	O(1)–Re(1)–S(1A)	109.1 (6)
S(1)–Re(1)–C(2)	135.0 (7)	C(1)–Re(1)–S(1A)	145.3 (8)
O(1)–Re(1)–C(2)	108.4 (9)	C(2)–Re(1)–S(1A)	77.9 (7)
C(1)–Re(1)–C(2)	74.7 (9)	Re(1A)–Re(1)–S(1A)	51.9 (2)
S(1)–Re(1)–Re(1A)	52.1 (2)	Re(1)–S(1)–Re(1A)	76.0 (2)
O(1)–Re(1)–Re(1A)	106.8 (6)	Re(1)–C(1)–C(10)	118.5 (16)
C(1)–Re(1)–Re(1A)	136.6 (6)	Re(1)–C(2)–C(20)	116.9 (15)

angle between planes defined by Re(1), S(1), S(1A) and Re(1A), S(1), S(1A): 143.6°

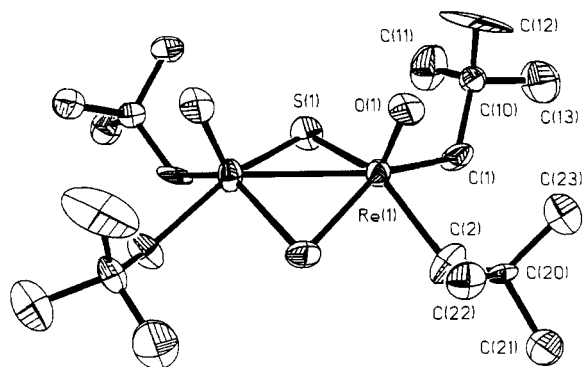
O(1)–Re(1)–Re(1A)–O(1A) dihedral angle: 7.1°

distance from Re(1) to best plane defined by S(1), S(1A), C(1), C(2): 0.70 Å

<sup>a</sup> Full details for both molecules appear in the supplementary material.

**Table III.** Fractional Coordinates ( $\times 10^4$ ) for *syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*syn*-3)

atom	x	y	z
Re(1)	536 (1)	1456 (3)	-192 (1)
S(1)	293 (3)	2240 (20)	869 (3)
O(1)	713 (7)	-1398 (19)	-314 (11)
C(1)	1355 (8)	2777 (50)	234 (11)
C(10)	1735 (9)	1358 (44)	889 (12)
C(11)	1617 (14)	2362 (63)	1579 (14)
C(12)	1729 (16)	-1205 (42)	847 (22)
C(13)	2346 (11)	2034 (59)	877 (19)
C(2)	803 (12)	3495 (40)	-1033 (11)
C(20)	974 (9)	2164 (38)	-1666 (10)
C(21)	1117 (12)	3992 (48)	-2201 (14)
C(22)	518 (10)	634 (45)	-2068 (12)
C(23)	1499 (10)	695 (48)	-1485 (14)
Re(2)	4436 (1)	2500	5100 (1)
S(2)	4797 (3)	1658 (18)	4111 (3)
O(2)	4228 (9)	5390 (24)	5087 (10)
C(3)	3959 (9)	1144 (42)	5863 (9)
C(30)	3998 (8)	2073 (36)	6651 (11)
C(31)	3439 (10)	1406 (47)	6883 (14)
C(32)	4489 (9)	1047 (49)	7147 (11)
C(33)	4041 (14)	4715 (46)	6642 (16)
C(4)	3746 (9)	708 (35)	4451 (11)
C(40)	3251 (8)	2108 (34)	4077 (10)
C(41)	3469 (10)	3684 (45)	3511 (12)
C(42)	2939 (11)	3622 (49)	4520 (13)
C(43)	2840 (12)	428 (51)	3663 (15)

**Figure 1.** ORTEP plot (30% probability level) of *syn*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*syn*-3) showing the atom-numbering scheme used in the tables.

*syn*-3 has virtual  $C_{2v}$  symmetry, and *anti*-3,  $C_{2h}$  symmetry. The rhenium centers in both isomers have square-pyramidal geometries

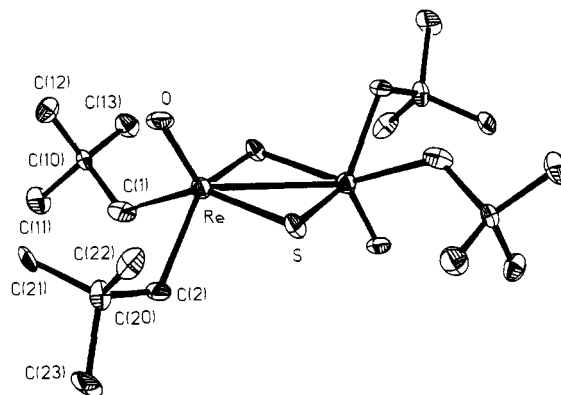
**Table IV.** Selected Bond Distances (Å) and Angles (deg) for *anti*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*anti*-3)

Bond Distances			
Re–S	2.289 (5)	Re–C(2)	2.200 (19)
Re–O	1.690 (13)	Re–Re(A)	2.871 (2)
Re–C(1)	2.173 (18)	Re–S(A)	2.247 (5)
Bond Angles			
S–Re–O	105.2 (4)	C(2)–Re–Re(A)	115.7 (5)
S–Re–C(1)	150.1 (5)	S–Re–S(A)	101.5 (1)
O–Re–C(1)	99.2 (6)	O–Re–S(A)	111.5 (5)
S–Re–C(2)	79.1 (5)	C(1)–Re–S(A)	85.0 (5)
O–Re–C(2)	108.5 (7)	C(2)–Re–S(A)	138.2 (5)
C(1)–Re–C(2)	76.9 (7)	Re(A)–Re–S(A)	51.4 (1)
S–Re–Re(A)	50.1 (1)	Re–S–Re(A)	78.5 (1)
O–Re–Re(A)	119.7 (4)	Re–C(1)–C(10)	125.4 (12)
C(1)–Re–Re(A)	128.6 (5)	Re–C(2)–C(20)	117.9 (12)

distance from Re to the plane defined by S, S(A), C(1), C(2): 0.70 Å

**Table V.** Fractional Coordinates ( $\times 10^4$ ) for *anti*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*anti*-3)

atom	x	y	z
Re	9496 (1)	1050 (1)	690 (1)
S	8864 (3)	-436 (7)	-635 (3)
O	9014 (11)	-429 (21)	1499 (8)
C(1)	9963 (14)	3852 (28)	1479 (12)
C(10)	10538 (14)	3803 (29)	2428 (11)
C(11)	10624 (17)	6182 (31)	2697 (14)
C(12)	9975 (15)	2530 (32)	3068 (11)
C(13)	11603 (15)	2928 (35)	2426 (13)
C(2)	8394 (15)	3493 (29)	225 (12)
C(20)	7354 (13)	3430 (30)	614 (11)
C(21)	7409 (16)	3992 (34)	1604 (12)
C(22)	6839 (12)	1394 (38)	434 (12)
C(23)	6766 (15)	5248 (36)	67 (14)

**Figure 2.** ORTEP plot (30% probability level) of *anti*-[Re( $\mu$ -S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (*anti*-3) showing the atom-numbering scheme used in the tables.

with the oxo ligand in the apical position and the basal plane defined by the neopentyl methylene carbons and bridging sulfido groups.

The terminal Re–O multiple-bond lengths for the two isomers are equivalent by the  $3\sigma$  criteria, as are the Re–C bond lengths. Both sets of distances are within the range observed in other related high-oxidation-state rhenium complexes.<sup>3,5–7</sup>

The Re–S distances in the two isomers are similar. There is, however, a statistically significant asymmetry in the two Re–S

- (5) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313. Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1988**, *7*, 2069. Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1489. Cai, S.; Hoffman, D. M.; Wierda, D. A. *Inorg. Chem.* **1989**, *28*, 3784.
- (6) Huggins, J. M.; Whitt, D. R.; Lebioda, L. *J. Organomet. Chem.* **1986**, *312*, C15.
- (7) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394; *Angew. Chem.* **1988**, *100*, 420.

bond distances of *anti*-**3** (2.289 (5) Å vs 2.247 (5) Å). All of the Re–S<sub>bridge</sub> distances are slightly shorter than those in d<sup>2</sup>–d<sup>2</sup> *anti*-[Re(μ-S)(η<sup>5</sup>-C<sub>5</sub>Me<sub>3</sub>O)]<sub>2</sub> (2.343 (2) and 2.329 (1) Å).<sup>8</sup>

The Re–Re single-bond distance in *anti*-**3** is slightly longer than the Re–Re distance in *syn*-**3**, 2.871 (2) Å vs 2.759 (3) Å, respectively, and both distances are significantly longer than those found in *syn*-[Re(μ-O)OR]<sub>2</sub> compounds (R = CH<sub>2</sub>CMe<sub>3</sub>, 2.606 (1) Å;<sup>2</sup> R = CH<sub>2</sub>CMe<sub>2</sub>Ph, 2.6116 (7) Å;<sup>6</sup> R = Me, 2.593 (1) Å).<sup>7</sup>

### Conclusion

We have prepared *syn*-Re<sub>2</sub>(μ-S)(μ-O)O<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> and *syn/anti*-[Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> from *syn*-[Re(μ-O)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and H<sub>2</sub>S. To our knowledge, these are the first examples of dinuclear Re(VI) sulfido compounds. We have also shown that *anti*-[Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> is converted to the thermodynamically more stable *syn* form in hydrocarbon and

pyridine solutions, perhaps through a mononuclear Re(O)(S)-(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> intermediate. The isomerization is reversible in pyridine. Synthetic efforts to trap the intermediate and redox studies of the [Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> compounds, which have shown that reversible reduction reactions are possible, are in progress.

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**Supplementary Material Available:** Textual details of the X-ray structure determinations, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles, an ORTEP plot of *syn*-[Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> generated from the other crystallographically independent Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> unit, and packing diagrams for *syn*-[Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and *anti*-[Re(μ-S)O(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (26 pages); structure factor tables (26 pages). Ordering information is given on any current masthead page.

(8) Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041.

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## Hydrolytic Polymerization of Rhodium(III). 1. Preparation, Solution Studies, and X-ray Structure of the Doubly Bridged Dimer [(H<sub>2</sub>O)<sub>4</sub>Rh(μ-OH)<sub>2</sub>Rh(OH<sub>2</sub>)<sub>4</sub>](dmtos)<sub>4</sub>·8H<sub>2</sub>O

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Several polynuclear Rh(III) species, formed on addition of excess base to solutions of [Rh(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>, have been separated by ion-exchange chromatography. Solution characterization studies, viz. charge (4+) and charge/Rh (2.1 (±0.1)), have confirmed that the doubly bridged hydrolytic dimer [(H<sub>2</sub>O)<sub>4</sub>Rh(μ-OH)<sub>2</sub>Rh(OH<sub>2</sub>)<sub>4</sub>]<sup>4+</sup> is one of the species formed. The UV–vis spectrum of the dimer shows an intense peak at 242 nm (ε ~ 1750 M<sup>-1</sup> cm<sup>-1</sup>), which is attributed to an OH<sup>-</sup> → Rh charge-transfer transition. Addition of dimer solutions to a pyridine buffer yields a fine yellow precipitate of the “active” dimer hydroxide of Rh(III), which consists of discrete dimer units and dissolves rapidly in acid to regenerate solutions of the hydrolytic dimer. Crystalline salts of the hydrolytic dimer of Rh(III) were obtained from concentrated dimer solutions prepared by dissolving the active hydroxide in either mesitylenc-2-sulfonic acid or *p*-toluenesulfonic acid. Electron microprobe and elemental analyses of the mesitylate salt were consistent with the composition [(H<sub>2</sub>O)<sub>4</sub>Rh(μ-OH)<sub>2</sub>Rh(OH<sub>2</sub>)<sub>4</sub>][(H<sub>3</sub>C)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>SO<sub>3</sub>]<sub>4</sub>·8H<sub>2</sub>O. The complex crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with cell parameters *a* = 17.981 (8) Å, *b* = 9.324 (3) Å, *c* = 17.367 (5) Å, β = 96.40 (3)°, and *Z* = 2. Least-squares refinement of the structure gave a final *R* value of 0.048 for 3151 observed reflections. The structure consists of double layers of the anions with the SO<sub>3</sub><sup>-</sup> groups pointing toward the complex cation. An extensive H-bonding network links the coordinated ligands, waters of crystallization, and SO<sub>3</sub><sup>-</sup> groups. The nonbonded Rh...Rh and O...O distances within the bridging moiety are 3.030 and 2.645 Å, respectively, while the O–Rh–O and Rh–O–Rh angles within the bridge are 82.20 and 97.40°, respectively. The Rh–O bridging distances (1.999 (5) and 2.023 (5) Å) are somewhat shorter than the terminal Rh–O distances (2.028 (5)–2.068 (5) Å). The uncertainty in each distance makes it impossible to ascertain whether the OH<sup>-</sup> bridges exert a significant trans influence.

### Introduction

The hydrolytic polymerization of Cr<sup>3+</sup> has been the subject of numerous investigations.<sup>1–10</sup> A considerable amount of important, and much needed, information has been obtained about the structure and properties of a series of hydrolytic oligomers, in-

cluding both kinetic and thermodynamic data. The kinetic inertness of Cr(III) has been an important factor in the development of this chemistry, since this has enabled the isolation of a series of Cr(III) oligomers. The success of this work has stimulated our interest in following the hydrolytic behavior of other kinetically inert metal centers and has led us to initiate investigations of Rh<sup>3+</sup>. The diamagnetic nature of this metal center is an attractive feature that offers the opportunity to follow hydrolytic processes by <sup>103</sup>Rh and <sup>17</sup>O NMR spectroscopy.

At present, very little is known about the hydrolytic polymerization of Rh(III), although the formation of polynuclear species has been postulated in the literature.<sup>11–14</sup> Cola<sup>11</sup> and Ayres and Forrester<sup>12</sup> observed changes in the properties of partially neutralized solutions of [Rh(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> with time, which they attributed to the formation of polynuclear species. Shukla<sup>13</sup> in electrophoretic studies of the conversion of Rh(OH)<sub>3</sub>·*x*H<sub>2</sub>O into [Rh(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> obtained evidence for species (possibly polynuclear) that were of

- (1) (a) Ardon, M.; Stein, G. *J. Chem. Soc.* **1956**, 2095. (b) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. (c) Ardon, M.; Linenberg, A. *J. Phys. Chem.* **1961**, *65*, 1443. (d) Kolaczowski, R. W.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322.  
(2) (a) Thompson, M. E.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279. (b) Finholt, J. E.; Thompson, R. E.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 4151. (c) Thompson, G. Ph.D. Thesis, Lawrence Radiation Report UCRL-11410, University of California, Berkeley, CA, 1964.  
(3) Stünzi, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145.  
(4) Stünzi, H.; Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1984**, *23*, 2160.  
(5) Spiccia, L.; Marty, W. *Inorg. Chem.* **1986**, *25*, 266.  
(6) Rotzinger, F. P.; Stünzi, H.; Marty, W. *Inorg. Chem.* **1986**, *25*, 489.  
(7) Spiccia, L.; Stoeckli-Evans, H.; Marty, W.; Giovanoli, R. *Inorg. Chem.* **1987**, *26*, 474.  
(8) Spiccia, L.; Marty, W.; Giovanoli, R. *Inorg. Chem.* **1988**, *27*, 2660.  
(9) Stünzi, H.; Spiccia, L.; Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1989**, *28*, 66.  
(10) Merakis, T.; Spiccia, L. *Aust. J. Chem.* **1989**, *42*, 1579.

- (11) Cola, M. *Gazz. Chim. Ital.* **1960**, *90*, 1037.  
(12) Ayres, H. G.; Forrester, S. J. *J. Phys. Chem.* **1959**, *63*, 1979.  
(13) Shukla, S. K. *Ann. Chem.* **1961**, 1383.  
(14) Moszner, M.; Ziolkowski, J. *J. Inorg. Chim. Acta* **1988**, *145*, 299.